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XVIII. *The Lattice Constants of the Elements.*

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(1) INTRODUCTION.

EVER since the introduction of the methods of X-ray crystal analysis, great interest has been aroused by the problem of the factors affecting the interatomic distances, and lattice constants of the different structures. Attention has been concentrated chiefly upon the interatomic distances in salts, and particularly in the alkali halides, and for these W. L. Bragg[1] has deduced a series of atomic or "ionic radii," which give consistent results when applied to the halides, and which can in many places be applied to more complicated structures. Recently Pauling[2] has used the principles of the new quantum mechanics to deduce ionic radii for the rock-salt type of structure, and the values obtained are in good agreement with those of W. L. Bragg, and explain certain abnormalities which are found when the structure involves the "contact" of like ions, instead of the more usual "contact" of oppositely-charged ions. In the method used by Pauling, the electrons in the outermost shell of the ions are treated as though they were in quantized orbits surrounding a nucleus of charge $(Ze-s)$, where Z

* Communicated by Prof. W. L. Bragg, F.R.S.

is the atomic number of the ion, and "s" is the so-called screening constant, to allow for the effect of the inner shells of electrons.

For the interatomic distances in metallic crystals detailed investigations have been made by Goldschmidt[3], who has emphasized the importance of the coordination number—*i. e.*, the number of atoms surrounding the particular atom under consideration. The majority of the metallic elements have structures with coordination number 12 (face-centred cubic, and hexagonal close-packed structures), or 8 (body-centred cubic), and Goldschmidt has deduced a series of "atomic radii" for metallic crystals in which the coordination number is 12. In cases where the element crystallizes with a different structure, the appropriate "atomic radius" is deduced from an alloy of the metal in which the structure has coordination number 12. These methods are open to the criticism that rather indiscriminate use is made of both solid solutions and intermetallic compounds, and since almost all the metals concerned are of variable valency, it is by no means certain that the atoms (or ions) are always in the same state in the different structures.

Up to the present, however, the atomic or ionic radii have been given as more or less empirical constants, and little is known of the laws which connect them with the atomic structures. In the present paper we shall describe some relations which have been found in this connexion for the interatomic distances in the crystals of the elements and shall discuss their significance. The only previous reference which has been found to work of this kind is a paper by Davey[4], describing a law of atomic radii, according to which the ratio of the atomic radii of any two members of a given group in the Periodic Table (say chromium and tungsten in Group VI.) is the same as the ratio of the atomic radii of the corresponding members of another group (say vanadium and tantalum in Group V.). As we shall see later, this law is not strictly true in all cases, although it is accurate for some groups, but it is curious that it was not investigated further.

(2) General Considerations.

In order to appreciate the laws underlying the lattice constants, it is advisable to consider briefly what is to be expected on theoretical grounds. It is well known that

the atoms of the different elements are built up in such a way that, as we go down the Periodic Table, each step results in the addition of one unit charge to the nucleus, and one extra-nuclear electron in order to keep the atom as a whole neutral. The extra-nuclear electrons in the *free atoms* then arrange themselves into definite shells characterized by the principal and subsidiary quantum numbers, and the periodic relations are the result of the fact that as each shell of electrons becomes completely filled, a new shell begins, and the process repeats itself. The presence of both the A and the B sub-groups, and of the rare-earth elements, is due to the fact that in the shells of higher quantum number, groups of 8 or 18 electrons have a provisional stability, and later expand into completed group of 18 or 32 electrons respectively. The result of this process is that the *free atoms* of the elements of any one sub-group have, except occasionally with high quantum numbers, the same number of electrons in the outermost shell (valency electrons), and, except as regards the first Short Period, they have the same number of electrons in the outermost shell but one. Thus all the alkali metal atoms have one-valency electron surrounding a shell of 8, except in the case of lithium, where the one-valency electron surrounds a completed shell of 2 electrons. Similarly in a group such as VI. A., the atoms of the three metals, chromium, molybdenum, and tungsten, each have 2-valency electrons surrounding an incomplete group of 12 in the outermost shell but one.

In the crystals of the solid elements it seems reasonable to suppose that it is the valency electrons which are responsible for the cohesive forces, except in Group O (the inert gases), where no such electrons are available. We have therefore to distinguish between those electrons responsible for the binding forces, and those which remain attached wholly to one atom or "ion." For convenience we shall denote by n the principal quantum number of the outermost shell of electrons remaining attached to the atomic cores or ions; since these electrons are attached to one atom only in the crystal, the values of n will be the same as those of the free atoms. Thus, in the alkali group, $n=1, 2, 3 \ldots$ for lithium, sodium, potassium. With the metals of variable valency in the middle of the long periods, it does not, of course, necessarily follow that the number of electrons in the outermost shell of the atomic

core or ion in the solid crystal is the same as that in the corresponding shell of the free atom.

We may first consider the nature of the repulsive forces which hold the atoms apart, and it seems reasonable to suppose that these will be determined principally by the outermost shell of electrons remaining attached to the atomic cores. In so far as these repulsive forces depend upon the symmetry, or the number of electrons in the outermost shell, they may be expected to be of a similar nature in the elements of any one sub-group, and to be a function of the quantum numbers n. The forces will not, however, be the same as those for the corresponding quantum numbers of a hydrogen atom, for the charge on the nucleus (Ze) must be taken into account, since increase in Z decreases the "size" of an electron shell of given quantum number. The magnitude of the effect may of course depend upon the screening action of the inner electrons, as considered in the work of Pauling.

The nature of the attractive forces is however less certain. It has been shown by the present author [5] that in the later B sub-groups (Groups IV., V., VI., and VII. B) there is a tendency for the element to crystallize so that each atom has (8-N) neighbours, where N is the number of the group. This was interpreted as meaning that each atom completes an octet of electrons by sharing one electron with each of its neighbours, and it was suggested that the metallic bond of the normal metals was of a similar nature, except that one electron had to serve for more than two atoms. For the attractive forces the following alternatives appear possible:—(1) The valency electrons may move in quantized orbits in which the attraction is towards the nuclei of charge Ze, probably modified by the screening effect of the inner electrons. (2) The electrons may be attracted towards the ion as a whole (*e. g.* towards Na^+, Ca^{++}, etc.), but may still move in quantized orbits; this is simply an extreme case of (1). (3) The electrons may be attracted towards the ions as a whole, but move freely between the atoms instead of in quantized orbits as in (2). (4) The valency electrons may form a lattice of the static type proposed by Lindemann [6], or the more dynamic type of Lennard-Jones [9].

Since the interatomic distance (d) in the crystal is that at which the attraction and repulsion balance one another, we shall expect that, in any one sub-group, d will be given

by an expression in which Z exerts a continuous effect to make the distance smaller, whilst n appears as a discontinuous factor, making the distance larger as the successive shells of electrons are built up. This expectation is fulfilled in the *Law of the Sub-Groups* described in the next section. It is, however, desirable to take into account the temperature at which the interatomic distance shall be measured, and we have here adopted the policy of comparing the distances at one-half the characteristic temperature. The correction for expansion is, however, negligible except in the alkali and alkaline-earth sub-groups, and for γ iron.

(3) The Law of the Sub-groups.

The first law concerning the interatomic distances may be expressed in the following form :—

In any one sub-group of the Periodic Table, provided that the Co-ordination Number remains constant, the interatomic distance d *is given by the relation*

$$\frac{d}{n} = \left(\frac{1}{a\mathrm{Z}}\right)^x,$$

where n is the principal quantum number of the outermost shell of electrons remaining attached to the ions ;

Z is the atomic number ;

x is a constant which is the same for groups with the same number of electrons in the outermost shell of the atomic core or ion ;

a is a second constant which in some groups may be connected with the valency.

In the case of those groups in which the atomic cores contain an outer group of 8 electrons (the inert-gas group, the alkali and alkaline-earth groups, and the titanium sub-group) the value of x is very nearly $\frac{1}{3}$, so that the law here becomes approximately $\frac{d^3}{n^3} = \frac{1}{a\mathrm{Z}}$.

But as the outer group of 8 electrons develops into an 18 group, the value of x increases to about 0·39--0·40. This law implies that if log $\frac{d}{n}$ be plotted against log Z, a straight line will be obtained, and figs. 1 and 2 show how

well this is established. The only point to be noted here is that, in Group IV., the elements carbon and silicon give values of d lying on the straight line through the titanium family, in spite of the fact that the coordination numbers are different, being 4 for carbon and silicon, and 12 for the

Fig. 1.

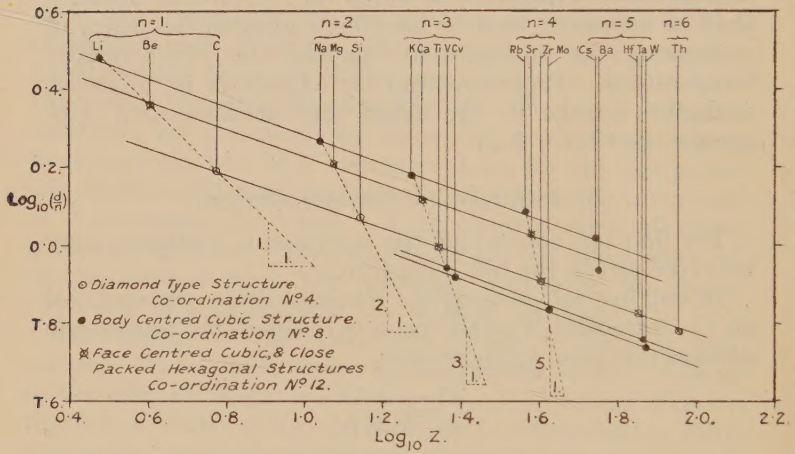
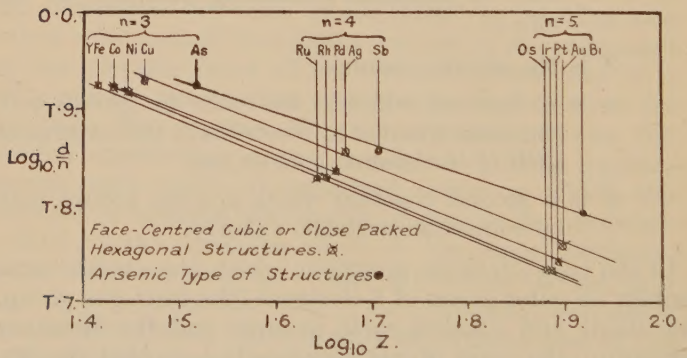


Fig. 2.



titanium sub-group. The significance of this is discussed later. The law suggested by Davey (*loc. cit.*) would require all the lines to be exactly parallel, but it can be seen that this is not strictly true. In the next section we shall discuss the accuracy with which the law holds.

Space does not enable a detailed review to be given of the experimental data which have been employed, but, in

general, use has been made of the data in the International Critical Tables, and those collected by Elam [8], except where these values have been corrected by later and more accurate work. The principal exceptions in this connexion are the results of Simon and Vohsen [9], Posnjak [10], Clark [11], and Ebert and Hartman [12] for the alkali and alkaline-earth metals, of Nazza and Nasini [13] for nickel, and of Natta and Nasini [14] for solid xenon *.

In order to reduce the interatomic distances to those at one-half the characteristic temperatures, the values of the latter have been taken from the paper by Biltz [15], whose data were recalculated by Lewis [16]. Use was also made of a paper by Allen [17], and in one or two cases it was necessary to estimate the characteristic temperature by interpolation on the periodic curve given by Biltz.

For the coefficients of expansion, the values given in the International Critical Tables were used. In some cases the coefficient is not given for low temperatures, and here the tendency is for the results to be over-corrected, when the characteristic temperatures are very low, and the values estimated for the alkali and alkaline-earth metals may be in error by ·01 Å. on this account. The only metal for which any real doubt exists is γ-iron, for which the experimental value for the interatomic distance is 2·566 Å. at 1373° K., and the estimated value at one-half the characteristic temperature is 2·52 Å., but cannot be looked upon as entirely reliable. In one or two cases where the coefficients of expansion were not available, these were estimated from those for metals occupying neighbouring places in the Periodic Table. The corrections introduced in this way are, however, negligible except for the alkali and alkaline-earth groups, and for γ-iron. The calculations have been carried out by means of four-figure logarithms, the fourth figure being dropped at the finish.

The majority of the elements crystallize in the diamond type, body-centred cubic, face-centred cubic, or close-packed hexagonal structures, in which each atom has four, eight, or twelve neighbours at an equal distance, which is taken as the inter-atomic distance. There are, however, some metals with the close-packed hexagonal structure, but with an axial ratio $a/c = 1{\cdot}59$, or slightly less than that

* For molybdenum the lattice constant, according to Davey [18], is $a = 3{\cdot}14$, and the value 3·41 given in Elam's paper is apparently a misprint.

corresponding to close-packed spheres. In such cases we give the values a and b of the major and minor axes of the oblate spheroid, to the close packing of which the structure corresponds, and we take the inter-atomic distance as that given by the value of a. The reason for this is that in the case of cobalt, which crystallizes both in a face-centred cubic form and in a close-packed hexagonal structure of axial ratio 1·59, it is the value of a which agrees with the interatomic distance in the face-centred cube. This point is discussed later.

1. *Group I. A. The Alkali Metals.*

As can be seen from fig. 1, all five alkali metals lie approximately on one straight line, in spite of the fact that in lithium the underlying ion contains a group of only two electrons, whereas, in all the other metals, the outer shell of the ion contains a group of eight. This is in many ways rather striking, and supports the conclusion of Pauling that completed shells of electrons are spherically symmetrical. Taking the group as a whole, the equation deduced from the graph is

$$\frac{d}{n} = \left(\frac{1}{\cdot 01637\,Z}\right)^{\cdot 362} = \frac{4\cdot 435}{Z^{\cdot 362}},$$

and Table I shows the agreement between the calculated and observed values. The maximum error here is ·05 Å. Close examination shows, however, that the last four alkali metals lie on a very much better straight line, indicating that lithium is not exactly equivalent to the remaining four, and this, of course, is only to be expected, since a group of two electrons can hardly behave in exactly the same way as one of eight. For the last four alkali metals the equation is

$$\frac{d}{n} = \left(\frac{1}{\cdot 0157Z}\right)^{\cdot 344} = \frac{4\cdot 175}{Z^{\cdot 344}},$$

and Table II. shows the agreement between the calculated and observed values. The maximum error is now only ·03 Å., and owing to the uncertainty of the coefficients of expansion there is an error of ·01 Å. in the reduction of the interatomic distances for rubidium and cæsium to one-half the critical temperature, in additon to any error in the experimental values. The error is thus of the order 0·6 per cent

TABLE I.

Metal.	Calculated interatomic distance.	Interatomic distance at ½ characteristic temp.	Error.
Lithium	2·98	3·02	−·04
Sodium	3·72	3·67	+·05
Potassium	4·58	4·54	+·04
Rubidium	4·80	4·85–4·86	−·05
Cæsium	5·20	5·22–5·23	−·02

TABLE II.

Metal.	Calculated interatomic distance.	Interatomic distance at ½ characteristic temp.	Error.
Sodium	3·66 Å.	3·67	−·01
Potassium	4·55 Å.	4·54	+·01
Rubidium	4·82 (4)	4·85–4·86	−·03–·04
Cæsium	5·26 (4)	5·22–5·23	+·03–·04

2. *Group II. A. The Alkaline-earth Metals.*

The equation deduced from the graph is here

$$\frac{d}{n} = \left(\frac{1}{\cdot 02265 Z}\right)^{\cdot 35} = \frac{3\cdot 765}{Z^{\cdot 35}}$$

TABLE III.

Metal.	Calculated interatomic distance.	Interatomic distance at ½ critical temperature.		Error.
Beryllium	2·32	*a*. 2·29 *b*. 2·25	c.p. hexag.	+·03
Magnesium.....	3·16	3·20	c.p. hexag.	−·04
Calcium	3·96	3·91–3·92	f.c. cube.	+·04–·05
Strontium	4·22	4·26	f.c. cube.	−·04
Barium	4·60 for face-centred cube.	4·32	b.c. cube.	Body-centred cubic.

and Table III. shows the agreement between the calculated and observed values, the accuracy being of the order

1 per cent. In this group barium has the body-centred cubic structure with coordination number 8, and therefore lies markedly off the straight line referring to the other members.

3. *Group III. A.*

This group cannot be examined because the structures of the later members have not been determined. The position of aluminium is discussed later (Section 8).

4. *Group IV. A.*

We have already mentioned that in this group the values for carbon and silicon lie almost on the same straight line as those for the titanium sub-group, in spite of the difference in coordination number. Taken as a whole, the group shows the worst agreement with the straight-line law, but examination shows that the error is due almost entirely to the value for thorium, and that if this metal be omitted, the remaining five elements are almost exactly on a straight line, as can be seen from fig. 1. The equation for this line is

$$\frac{d}{n} = \left(\frac{1}{\cdot 0465(6)\mathrm{Z}}\right)^{\cdot 345} = \frac{2\cdot 882}{\mathrm{Z}^{\cdot 345}},$$

and Table IV. shows the agreement between the observed and calculated values. As in Group II., we take the a value for the inter-atomic distance in the close packed

Table IV.

Element.	Structure.	Calculated value of d.	d at ½ charact. temp.	Error.
Carbon	Diamond type.	1·55	1·54	+·01
Silicon	Diamond type.	2·32	2·35	−·03
Titanium	c.p. hex. $\frac{a}{c}=1\cdot 59$	2·98	$a=2\cdot 95$ $b=2\cdot 90$	+·03
Zirconium	,, ,,	3·23	$a=3\cdot 23$ $b=3\cdot 17$	·0
Hafnium	c.p. hex. $\frac{a}{c}=1\cdot 62$	3·30	$a=b=3\cdot 32$	−·02
Thorium	f.c. cube.	3·66	3·59	+·07

hexagonal structures with axial ratio 1·59 (see p. 224). The value for thorium lies distinctly off the straight line given for other elements, and the reason for this is discussed later (pp. 235, 236). The effect of the coordination number in this group is discussed in Section 6, in which it is shown that, to a higher degree of accuracy, the close-packed hexagonal metals titanium, zirconium, and hafnium probably form one straight line, from which carbon, silicon, and thorium diverge owing to differences in crystal structure, and in the number of electrons in the outermost shell of the core, and to a systematic deviation from the law for very large values of Z.

5. *Group V. A.* (*Body-centred Cubic.*)

In this group data are only available for vanadium and tantalum, so that the straight line law cannot be tested. The straight line through the two points gives the equation

$$\frac{d}{n} = \left(\frac{1}{\cdot 0628 Z}\right)^{\cdot 368} = \frac{2\cdot 769}{Z^{\cdot 368}}.$$

6. *Group VI. A.* (*Body-centred Cubic.*)

The three metals chromium, molybdenum, and tungsten give a very good straight line corresponding to the equation

$$\frac{d}{n} = \left(\frac{1}{\cdot 0675 Z}\right)^{\cdot 376} = \frac{2\cdot 755}{Z^{\cdot 376}}.$$

TABLE V.

Metal.	Calculated interatomic distance.	Interatomic distance at ½ critical temperature.	Error.
Chromium	2·50	2·49	+·01
Molybdenum ...	2·70	2·72	—·02
Tungsten	2·73	2·73	0

Table V. shows the agreement between the observed and calculated values.

7. *Group VII. A.*

The only metal investigated in this group is manganese, which has complex structures for its different allotropic forms. The straight-line law cannot therefore be tested.

8. *Group VIII.* (*a*). *Iron, Ruthenium, Osmium.*

In this group the position is obscured by the fact that ruthenium and osmium have close-packed hexagonal structures with coordination number 12, whilst the face centred allotropic form of iron, with the same coordination number, is stable only at very high temperatures, and the correction for expansion becomes considerable and speculative, although the error is not likely to be more than ·02 or ·03 Å. The close-packed hexagonal structures have axial ratio 1·59, and both major and minor axes of the oblate spheroid are given in Table VI., which shows the agreement with value calculated from the equation

$$\frac{d}{n}=\left(\frac{1}{\cdot 05998Z}\right)^{\cdot 404}=\frac{3\cdot 116}{Z^{\cdot 404}}.$$

Table VI.

Metal.	Calculated interatomic distances.	Interatomic distances at ½ characteristic temp.	Error.
Iron (γ)	2·51	? 2·52?	—·01?
Ruthenium.....	2·70	$\left\{\begin{matrix}a=2\cdot 69\\b=2\cdot 64\end{matrix}\right\}$	+·01
Osmium.....	2·71	$\left\{\begin{matrix}a=2\cdot 71\\b=2\cdot 66\end{matrix}\right\}$	0

As in the case of beryllium the straight line has been drawn to give the best agreement with the value of a in the close-packed hexagonal structure. The errors are negligible.

9. *Group VIII.* (*b*).

The equation in this case is

$$\frac{d}{n}=\left(\frac{1}{\cdot 05689Z}\right)^{\cdot 418}=\frac{3\cdot 314}{Z^{\cdot 418}},$$

and the straight line law is fulfilled almost exactly, as can be seen from Table VII.

TABLE VII.

Metal.	Calculated interatomic distances.	Interatomic distances at ½ characteristic temp.	Error.
α Cobalt.....	2·51	2·51 face-centred cube	0·00
β Cobalt.....	...	$\left\{\begin{matrix} a=2\cdot51 \\ b=2\cdot46 \end{matrix}\right\}$ hex. c.p.	
Rhodium	2·70	2·70 f.c. cube	0·00
Iridium	2·70	2·70 f.c. cube	0·00

10. *Group VIII. (c).*

The equation here is

$$\frac{d}{n} = \left(\frac{1}{\cdot 05808Z}\right)^{\cdot 39} = \frac{3\cdot035}{Z^{\cdot 39}},$$

and the straight-line law is fulfilled almost exactly as can be seen from Table VIII.

TABLE VIII.

Metal.	Calculated interatomic distance.	Interatomic distance at ½ characteristic temp.	Error.
Nickel.....	2·48	2·48	0·00
Palladium	2·73	2·73	0·00
Platinum	2·77	2·76	+0·01

11. *Group I.B.*

The equation here is

$$\frac{d}{n} = \left(\frac{1}{\cdot 05105Z}\right)^{\cdot 393} = \frac{3\cdot219}{Z^{\cdot 393}},$$

and the agreement with the straight-line law is not so good as in the preceding groups, the error being as much as 1 per cent., as can be seen from Table IX.

TABLE IX.

Metal.	Calculated interatomic distance.	Interatomic distance at ½ characteristic temp.	Error.
Copper	2·57	2·55	+·02
Silver	2·84	2·87	−·03
Gold	2·89	2·87	+·02

12. *Groups II. B and III. B.*

In these groups the crystal structures are irregular so that the law cannot be tested, and as the author has previously suggested (5) the evidence is that, in some cases, the metals are not fully ionized in the solid crystal. Thus indium and thallium are probably only singly ionized, and so have much larger interatomic distances than the preceding univalent metals silver and gold.

13. *Group IV. B.* (*Diamond Structure.*)

In Group IV., as we have already explained, carbon and silicon give $\frac{d}{n}$ values which fit on to the line for the titanium sub-group, in spite of the difference in co-ordination number. The four elements with the diamond type of structure (carbon, silicon, germanium, and grey tin) do form a rough straight line, and the equation for this is

$$\frac{d}{n} = \left(\frac{1}{\cdot 0515 Z}\right)^{\cdot 40} = \frac{3\cdot 275}{Z^{\cdot 40}}$$

which gives 1·60, 2·28, 2·46, and 2·74 A. as compared with the experimental values of 1·54, 2·35, 2·43, and 2·79 for carbon, silicon, germanium, and grey tin respectively. The agreement is thus approximate only, and this, of course, is to be expected, since we have three different electronic groupings in the underlying ions—2 for carbon, 8 for silicon, and 18 for germanium, and grey tin.

The straight line through the two points for germanium and grey tin with the (18) group of electrons corresponds to the equation

$$\frac{d}{n} = \left(\frac{1}{\cdot 0588 Z}\right)^{\cdot 33} = \frac{2\cdot 571}{Z^{\cdot 33}}.$$

If the experimental values for germanium and grey tin be plotted in fig. 1, it will be found that they lie distinctly below the straight line given by the elements of Group IV. A.

14. *Group V. B.* (*Arsenic, Antimony, Bismuth.*)

These elements crystallize so that each atom has three close neighbours, and thus satisfy the (8-N) rule indicating

a simple co-valent bond. The law of the sub-groups is, however, still satisfied, the equation being

$$\frac{d}{n} = \left(\frac{1}{\cdot 04753Z}\right)^{\cdot 323} = \frac{2\cdot 569}{Z^{\cdot 323}},$$

and as can be seen from Table X. and fig. 2, a very fair straight line is obtained.

TABLE X.

Metal.	Calculated interatomic distance.	Interatomic distance d, at $\frac{1}{2}$ characteristic temp.	Error.
Arsenic	2·49	2·51	—·02
Antimony	2·89	2·86	+·03
Bismuth	3·08	3·09	—·01

We shall consider later (p. 242) the very interesting relations found for the second distances of approach in these structures.

15. *Group VI. B.* (*Selenium, Tellurium.*)

In this group only two members have been investigated so that the linear relation cannot be tested. The structures are such that each atom has two close neighbours, and four at a greater distance, so that the (8-N) rule is fulfilled, indicating simple covalent bonds. For the closest distance of approach (d), the straight line through the two points corresponds to the equation

$$\frac{d}{n} = \left(\frac{1}{\cdot 0944Z}\right)^{\cdot 21}.$$

The slope is thus markedly different from all the preceding groups, and the reason for this is clearly that in Group VI. B each atom has six valency electrons and shares two with each of two neighbours, so that four of the valency electrons remain attached to each atomic core, and the repulsive forces are no longer the result of the n electrons alone.

16. *Group O.* (*Inert Gases.*)

The structures of krypton and xenon have now been determined, and it is interesting to note that the line

through the two points which are thus available has almost exactly the same slope as that for the alkali, alkaline earth, and titanium sub-groups in which the underlying ions have the inert gas structure. The straight line for the inert gas group deduced from these two values gives the equation

$$\frac{d}{n} = \left(\frac{1}{\cdot 02735 Z}\right)^{\cdot 348} = \frac{3\cdot 498}{Z^{\cdot 348}}.$$

(4) The Variations of the Constant x.

Table XI.

Group.	Value of x.
O	·348
I. A	·344*
II. A	·35
IV. A	·345
V. A	·368
VI. A	·376
VIII. (*a*)	·404
VIII. (*b*)	·418
VIII. (*c*)	·39
I. B	·393
IV. B	·33†
V. B	·323
VI. B	·21

In Table XI. are summarized the values for the constant x in the equations $\frac{d}{n} = \left(\frac{1}{aZ}\right)^x$ for the different groups. It will be seen that these are constant at 0·34–0·35 for the four groups with the inert gas type of ion, and that this constant value is very nearly $\frac{1}{3}$ (0·33). The value of x then increases steadily to a maximum of 0·418 in Group VIII. *b*. Close examination reveals certain additional minor regularities. Thus the slope of the line through germanium and grey tin is 0·33, and is identical with that through copper and silver. The value 0·39 given for Group I. B is higher than this, because the line is drawn so as to include the value for gold. These differences are clearly due to the difference in the screening effects caused

* Taken from the equation for the last four alkali metals.
† Taken from the line through germanium and grey tin.

by the filling up of the inner quantum shells which takes place during the rare earth elements.

(5) The Variation of the Constant a.

In Table XII. are summarized the values of the constant a in the equations $\frac{d}{n} = \left(\frac{1}{a\bar{Z}}\right)^r$ for the different groups, the figures after each group giving the coordination number, which, of course, affects the value of a. It will be noted that in Groups II. A and IV. A which have the same coordination number, the values of a are almost as 1 : 2,

Table XII.

Group.	Value of $a \times 10^2$
O (12)	2·74
I. A (8)	1·57
II. A (12)	2·27
IV. A (12)	4·66
V. A (8)	6·28
VI. A (8)	6·75
VIII. *a* (12)	6·00
VIII. *b* (12)	5·69
VIII. *c* (12)	5·81
I. B (12)	5·11
IV. B (4)	5·88
V. B complex	4·74
VI. B complex	9·44

suggesting that in the early A groups, the value of a is proportional to the valency, provided that the coordination number remains the same. If this were so we should expect that on plotting $\log \frac{d}{n}$ for the metals of Groups I. A, II. A, and IV. A against log Z, log 2Z, and log 4Z respectively, all the metals with the same coordination number should lie on the same straight line. For the metals with coordination number 12 in Groups II. A and IV. A this condition is satisfied to an approximation, but, on the other hand, barium, with the body-centred cubic structure, lies distinctly above the straight line corresponding to the alkali metals, the difference being equivalent to about 0·3 Å. From this we may conclude that the constant a is not strictly proportional to the valency.

(6) The Effect of Coordination Number and Crystal Structure.

Before discussing the significance of the laws described above, it is advisable to consider briefly what evidence the equations give for the effect of coordination number and structure upon the interatomic distances. We shall here confine ourselves solely to the evidence from the elements, and shall not deal with the figures obtained from alloy structures.

We have already seen that in Group II., the straight line obtained for the first four members would give the value of d for barium with coordination number 12 as 4·60 Å., as compared with the experimental value 4·32 Å. for the body-centred structure with coordination number 8. This gives the ratio

$$d(12) : d(8) = 1{\cdot}06 : 1.$$

In this group the equation is subject to a comparatively large error of from ·03 to ·04 Å., so that the extreme possible values for $d(12)$ are 4·56 and 4·64, the corresponding values of the ratio $d(12) : d(8)$ being 1·05 : 1 and 1·07 : 1. This means that the change from coordination number 12 to coordination number 8 results in a contraction of $5\frac{1}{2}$ per cent., which is considerably greater than that deduced by Goldschmidt from his work on alloy structures.

The second case in which we can compare the same effect is that of iron, which crystallizes in both body-centred and face-centred forms, but here we meet with the difficulty in reducing the value for iron from that obtained at very high temperatures. If we allow an error of ±·02 Å. in our value 2·52 Å., we have the value for $d(12)$ as lying between 2·50 Å. and 2·54 Å., whilst $d(8)$ from the experimental data is 2·475 Å., so that the extreme values for the ratio $d(12) : d(8)$ are 1·01 and 1·025. This is of the same order as the change deduced by Goldschmidt, *but it is, of course, subject to the assumption that the iron atom is in the same state in both structures*, which in the opinion of the present author is improbable. This difficulty does not arise in the case of barium, for the whole of the evidence is that this element is divalent in the crystal. But although the data for iron may to some extent be affected by a change in the state of the atom, a very marked difference would have to occur in order to increase the ratio to the value 1·06 deduced for

the values for barium. On the other hand, in the case of chromium the value of d in the body-centred cubic modification is 2·49 Å., and, in the close-packed hexagonal structure, 2·71 Å., so that the ratio $d(12) : d(8) = 1{\cdot}09 : 1$. This is even greater than the ratio deduced for barium, so that the evidence is that the ratio is not constant in the different groups.

This conclusion is confirmed by the fact, which we have already mentioned, that in Group IV. the points for carbon and silicon lie very nearly on the straight line for the titanium sub-group, in spite of the difference in co-ordination number. Careful examination shows that titanium, zirconium, and hafnium form a slightly better straight line if carbon and silicon be omitted, the equation in this case being

$$\frac{d}{n} = \left(\frac{1}{\cdot 04688Z}\right)^{\cdot 34},$$

which gives 1·54, 2·31, 2·97, 3·23, and 3·31 Å. for the values of d in carbon, silicon, titanium, zirconium, and hafnium as compared with the experimental values 1·54, 2·35, 2·95, 3·23, and 3·32 Å. respectively. But the difference between this and the previous equation for the group as a whole is very slight. It will be noted that the greatest difference (−·04 Å.) is shown by silicon, so that it is possible that the almost negligible difference for carbon is due to opposing effects of change in coordination number, and change in the number of electrons in the outermost shell of the atomic core. But there is no doubt that, in this case, the change from coordination number 4 to one of 12 affects the value of d by only about 1 per cent., and is much less important than the number of electrons in the outermost shell of the ion, as is shown by the comparatively large errors (·05–·07 Å.) if the values are plotted for the four elements carbon, silicon, germanium, and grey tin, which have the same crystal structure, but different numbers of electrons in the outermost shell. The significance of this is discussed later. The conclusion is opposed to that of Goldschmidt, and, in the opinion of the author, this is probably due to the fact that, in the alloy structures considered by this worker, the atoms were not always in the same state.

There is, however, no doubt that the value for thorium deviates from the straight line given by the other members

of the group, and this is probably due to the gradual breakdown of the law for high values of Z (see (8)), whilst it is also perhaps possible that the direct comparison of the face-centred cubic and close-packed hexagonal structures is not strictly justified. We have assumed so far that those two structures can be compared directly, since they both have the same coordination number, but it is unlikely that the structures are exactly equivalent, since, if it were just a matter of chance which structure was formed, we should expect many metals to crystallize in both forms, whereas, actually, cobalt and chromium are the only metals which show this type of allotropy. Apart from this, we have, as explained previously, compared the distance in the face-centred cubic structures with the a values in the close-packed hexagonal structures of axial ratio 1·59, and this is, of course, rather arbitrary. In Group II. A close examination shows that the line through the points for beryllium and magnesium with close-packed hexagonal structures lies above that for the face-centred cubic metals of the same group, so that it is possible that the two are not really directly comparable.

To summarize, the evidence is that change in co-ordination number does not cause the same percentage contraction in the different groups, and that in Group IV. the effect of coordination is comparatively slight.

(7) Relations in the Periods.

In the preceding sections we have seen how, in each sub-group, the interatomic distances are given simply by equations of the type $\frac{d}{n} = \left(\frac{1}{aZ}\right)^x$, but except for noting that the value of a was roughly doubled in passing from Group II. A to IV. A, we have not attempted to show how the different lines are related. This problem is much more complicated owing to the fact that in passing along *any one period* the coordination numbers and the numbers of electrons in the outer shells of the ions change, whereas in passing down any one sub-group these factors in general remain unaltered. It has, however, been possible to trace some very interesting relations.

(a) *In the First Short Period the interatomic distance is, to an approximation, simply inversely proportional to the*

atomic number. Thus, assuming the experimental value $a=2{\cdot}29$ Å. for beryllium (Z=4). we should expect the values of d for lithium (Z=3) and carbon (Z=6) to be $\frac{2{\cdot}29\times4}{3}=3{\cdot}05$ Å., and $\frac{2{\cdot}29\times4}{6}=1{\cdot}53$ Å., as compared with the experimental values 3·02 Å. and 1·54 Å. The difference in the case of lithium is in the direction to be expected from the different coordination numbers, whilst as we have already shown in (6) the evidence is that the coordination number has little effect in Group IV.

This relation is of interest in two ways. In the first place, considered purely empirically, it enables us to generalize the three equations for Groups I. A, II. A, and IV. A. Thus if we assume the experimental value for beryllium, we can calculate the values for lithium and carbon from the fact that in the First Short Period $d\sim\frac{1}{Z}$, and then, knowing that the three straight lines connecting $\log\left(\frac{d}{n}\right)$ and log Z have approximately the same slope of about 0·35, we can in effect calculate the interatomic distances in all the elements of those three sub-groups, except barium, by assuming only two constants. A very satisfactory degree of generalization is thus obtained, although there is some loss of accuracy owing to the fact that lithium does not lie exactly on the straight line for the other alkali metals.

In the second place, this relation confirms the conclusion that, when the screening effects due to inner shells of electrons are absent, the interatomic distance is simply inversely proportional to the atomic number. This can readily be seen from fig. 1, where it will be noted that the points for lithium, beryllium, and carbon lie on a straight line inclined at 45° to the axes.

(b) *In the Second, Third, and Fourth Periods* some very curious relations exist, and, although these are really included in the Law of the Sub-Groups, and the relation (*a*) above, it may be well to point them out directly. As we have shown above, the data indicate that the coordination number has comparatively little effect in Group IV. A, so that the value for silicon can be compared directly with that of magnesium, whilst, later, comparison

can be made between titanium and calcium, and between zirconium and strontium, where the coordination number is 12 throughout. On the other hand, the values for the alkali metals are not necessarily strictly comparable with these, since we have shown that a contraction occurs in Group II. A, when the structure changes from coordination number 12 to 8, and the same may be expected in Group I. A.

The curious fact now emerges that, whilst in the First Period, on passing from Group II. A to IV. A, the interatomic distance varies as $\frac{1}{Z}$, in the Second Period it varies as $\frac{1}{Z^2}$ and, in the Third Period as $\frac{1}{Z^3}$.

This implies that the lines in fig. 1 connecting the first few elements in any one period make angles whose tangents are 1, 2, and 3 in the first three periods, and this is indicated in fig. 1, but for accuracy it is necessary to redraw the figure to a suitable scale, and if this be done it will be found that the relation is satisfied with quite remarkable accuracy in passing from Group II. to Group IV., although not always so accurately from Group I to Group II.

Thus in the Second Period the interatomic distances in sodium, magnesium, and silicon are 3·67, 3·20, and 2·35, or as 1·56 : 1·36 : 1. The inverse squares of the atomic numbers are as $\frac{1}{11^2} : \frac{1}{12^2} : \frac{1}{14^2} = 1{\cdot}62 : 1{\cdot}36 : 1$.

In the Third Period, the interatomic distances in potassium, calcium, and titanium are 4·54, 3·91, and 2·95, or as 1·54 : 1·33 : 1. The inverse cubes of the atomic numbers are as $\frac{1}{19^3} : \frac{1}{20^3} : \frac{1}{22^3} = 1{\cdot}55 : 1{\cdot}33 : 1$.

On the other hand, in the Fourth Period the interatomic distances do not vary as $\frac{1}{Z^4}$, but nearly as $\frac{1}{Z^5}$, although the agreement is not so good as in the previous Periods. The interatomic distances in rubidium, strontium, and zirconium are 4·85, 4·26, and 3·23 A., or as 1·50 : 1·32 : 1, whilst the inverse fifth power of the atomic numbers are as $\frac{1}{37^5} \quad \frac{1}{38^5} : \frac{1}{40^5}$ or 1·48 : 1·29 : 1. In the

Fifth Period, the fact that barium has a different coordination number from the other alkaline earth metals prevents a comparison from being made*. There is, however, no doubt that, as we proceed from Group I. to Group V., the interatomic distances vary almost exactly as $\frac{1}{Z}$, $\frac{1}{Z^2}$, and $\frac{1}{Z^3}$ in the first three Periods, and almost as $\frac{1}{Z^5}$ in the Fourth Period. All these relations are, of course, contained in the Law of the Sub-Groups and the relation (*a*) above, since these enable us to fix the positions of the three lines for Groups I., II., and IV. A, but the exact whole numbers involved in the terms $\frac{1}{Z}$, $\frac{1}{Z^2}$, $\frac{1}{Z^3}$ and $\frac{1}{Z^5}$ are of great interest, and are clearly connected with the screening effect, the jump from $\frac{1}{Z^3}$ to $\frac{1}{Z^5}$ coinciding with the building up of an (18) group in the inner shells of electrons.

It has not yet been found possible to extend the generalization beyond Group IV., and the reason for this is clearly that the outermost shell of the ion no longer contains the same number of electrons.

(8) Discussion.

The discovery of such clear quantum relations for the lattice constants of the elements is of interest, since it indicates how the quantum numbers of atomic structure may be introduced directly into problems connected with the solid state. The following points may now be discussed briefly.

1. *The Accuracy of the Law of the Sub-Groups.*

Reference to the previous tables shows that the divergences from the linear relations between log d/n and log Z, correspond to differences which rarely exceed 1 per cent., and which, in many sub-groups, are less than $\frac{1}{2}$ per cent. of

* The slope of the line through barium and cæsium is almost exactly 10, indicating a variation as $\frac{1}{Z^{10}}$ in this period, but the gradient is here very steep so that accuracy is lost.

the values of d. The deviations are, however, to some extent systematic, and may be classed as follows :—

(a) Except in Group IV., the effect of coordination number is important, and cannot be allowed for by a simple proportionality factor.

(b) The number of electrons in the outermost shell of the ion is important, and completed groups of 2, 8, and 18 electrons are not exactly comparable.

(c) There is a general tendency for the calculated values to be too small in the second short Period (Na, Mg, Si), and too great with very large values of Z (Th, Au).

It is clear, therefore, that the equation will eventually have to contain secondary quantum numbers or other correction factors. It is, however, thought undesirable to attempt to introduce correction terms of this kind until either it has been possible to place the law on a theoretical basis, which indicates the correction factor, or until the lattice constants are known to within ·005 Å. at corresponding temperatures for a number of groups, a condition which is not yet satisfied. At present, therefore, absolute agreement with the experimental values cannot be claimed, but in view of the fact that only the principal quantum number is being used in these equations, an error of from $\frac{1}{2}$ per cent. to 1 per cent. in the different groups must be considered as satisfactory.

2. *The Meaning of the Law*

It is possible to account for an equation of the type $\frac{d}{n} = \left(\frac{1}{aZ}\right)^r$ if we assume an attractive force varying as the inverse square of the distance, and a repulsive force varying as an inverse higher power, with a proportionality factor involving n and Z. In apparent agreement with this is the approximate doubling of the constant a in passing from Group II. A to IV. A, suggesting an attraction proportional to the charge on the ion. It seems improbable that this line of approach is correct for the following reasons : (1) There is no such contraction on passing from Group I. B to IV. B. (2) The value of d for barium is not given exactly by the equation for the alkali group with the constant a doubled. (3) The relations in the first short Period where the distance is simply inversely proportional

to the atomic number do not support the view that the charge on the ion is directly responsible for the contraction in passing from Group I. to Group IV. (4) Any explanation on these lines would, by the conventional analysis, require the compressibilities of the different elements in one sub-group to vary as d^4, and this is not the case.

In this connexion reference may be made to a paper by Thomas [19] on the calculation of atomic fields. In this work the atomic quantum numbers are not introduced, but the atom is treated as a nucleus surrounded by an atmosphere of electrons. The equations obtained are of such a nature that, if two atoms of atomic numbers Z_1 and Z_2 are compared, the expression for the potential at a distance d_1 from the centre of the first atom is simply related to that at a distance d_2 in the second atom, provided that $\frac{d_2}{d_1} = \left(\frac{Z_1}{Z_2}\right)^{\frac{1}{3}}$. There is a curious similarity between this conclusion and the simplified form of the Law of the Sub-Groups $\frac{d}{n} = \left(\frac{1}{aZ}\right)^{\frac{1}{3}}$, where the inverse cube root of the atomic number is again found.

3. *The Relations for the Group IV. Elements.*

We have already seen that the values for carbon and silicon give points lying on the straight line through the titanium-zirconium group in spite of the difference in co-ordination number. This is of particular interest in view of the fact that titanium, although it has a close-packed structure, shows the phenomenon of a minimum electrical resistance at 112° C., an effect which is characteristic of many of the elements of the B sub-groups, which obey the (8-N) rule indicating the presence of simple covalent bonds in the crystal. The existence of a minimum electrical resistance is quite to be expected in those structures which are the result of covalent electronic bonds where each valency electron is shared between two atoms, since, on raising the temperature, we may expect that electrons will first be liberated with a fall in resistance, but that this effect will be counterbalanced by the steadily increasing amplitudes of the atomic vibrations, which increase the resistance in the usual way. But the occurrence of the effect in a metal with the normal close-packed structure is much more striking, and appears to indicate

that we have a continuous transition from the purely covalent type of bond in those elements obeying the (8-N) rule, through the intermediate linkage found for titanium, to the purely metallic bond in the normal metals. This supports the author's previous suggestion that the covalent and the metallic linkages are really of the same nature, and differ only in that a valency electron is shared between two atoms in a covalent structure, but serves for more than two atoms in a metal.

4. *The Inert Gas Group.*

One of the rather unexpected results in connexion with the interatomic distance in the elements is that the inert gases argon and xenon give smaller values of d (3·84 Å. and 4·37 Å.) than those for the following alkali metals potassium (4·56 Å.) and cæsium (5·22 Å.). At first it might be expected that the interatomic distances would be greater in the inert gases, because (*a*) the atomic numbers are less than those of the following alkali metals, and (*b*) the very low melting-points of the inert gases indicate a weak kind of binding. The probable explanation of this is that in the inert gases the atom is neutral, and has no valency electrons which can be shared. In the crystal of the alkali metal, on the other hand, the *ions* are bound together by the shared electrons, and, whilst this linkage is more stable thermally, the mutual repulsion of the positive ions makes the equilibrium distance greater.

5. *The Position of Aluminium.*

We have already noted that lack of experimental data prevents the law of the Sub-Groups being tested for Group III. A. If the isolated value for aluminium be inserted in fig. 1, it will be found that the value of d appears to be too high to fit in with the regular decrease from Group I. to Group IV. This suggests that aluminium is not fully ionized in the metallic crystal, and this conclusion is supported by many other facts such as the very small increase (8°) in melting-point in passing from magnesium to aluminium, irregularities in the sequence of photo-electric threshold frequencies, electrical conductivities per atom, etc.

6. *The Second Distances of Approach in the Arsenic Group.*

In the arsenic type of structure, each atom has three close, and three more distant, neighbours, and we have

already seen that, for the closest distances of approach, a very good straight line is formed when $\log \frac{d}{n}$ is plotted against log Z, the slope of this line being 0·32. If the second distances of approach (d^1) are plotted in the same way, a distinctly poor agreement with the linear law is found, and the slope of the best straight line through the three points is −0·46, *i. e.*, very much greater than in all the previous cases. These abnormalities are clearly due to the fact that in the Group V. Elements, each atom has five valency electrons of which only three are shared in order to complete the octet; thus leaving two unshared valency electrons attached to each ion. It seemed possible therefore that the unshared valency electrons were responsible for the repulsive zones which caused the second distances of approach, and the interesting fact was then found that if log Z were plotted, not against $\log \frac{d^1}{n}$, but against $\log \left(\frac{d^1}{n+1}\right)$—where $(n+1)$ gives the quantum number of the valency electrons—not merely was a much better straight line obtained, but the slope was −0·33, or almost exactly the same as that of the $\log \frac{d}{n}$/log Z curves for the closest distance of approach. If this is not a mere coincidence, it clearly suggests that the two different sets of interatomic distances are due to the two distinct shells of electrons, and this will, of course, explain why the two distances become more nearly equal as we pass from arsenic to bismuth, since the ratios $\frac{n}{n+1}$ approach unity as n becomes greater. But in Group VI. B (selenium and tellurium), where there are four unshared electrons per atom, this kind of relation does not hold.

9. Acknowledgments.

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The Old Chemistry Department,
The University Museum, Oxford,
May 1930.

XIX. *Glow Discharge in Hydrogen.*

By Dr. R. D. Rusk, *Mt. Holyoke College* *.

IT has been suggested by Richardson and Tanaka † that the glow which they obtained by a discharge in hydrogen at pressures below one-tenth of a millimetre is most probably caused by resonance of neutral molecules, because it has little or no relation to the distribution of the electric field. They also suggest that the glow probably arises as a result of excitation by radiation rather than by electron impact. Some measurements of the space potential have been made by Bramley ‡ in the region between the hot filament and the cold anode both for the striated and non-striated discharges. In the latter instance the potential distribution was found to be quite

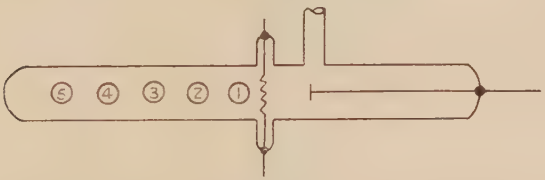
* Communicated by the Author.
† Proc. Roy. Soc. A. cvi. (1924).
‡ Phys. Rev. xxvi. (1925).

uniform except for the sharp drop at the cathode and a slight indication of a reverse field. In the present experiment these measurements of potential were extended into the region back of the hot filament and away from the anode.

The apparatus and method followed were essentially those of Bramley, except that different sets of readings were taken with both fixed and movable electrodes. The cold exploring electrode consisted in every instance of about a millimetre of number 26 platinum wire extending from the sealed tip of a glass tube.

The experimental tube, as shown in fig. 1, was two and a half centimetres in diameter, and the filament and anode were placed fifteen milimetres apart near the centre of the tube, which was about twenty centimetres long. The filament was an ordinary coated platinum wire, and the

Fig. 1.



The experimental tube with exploring electrodes.

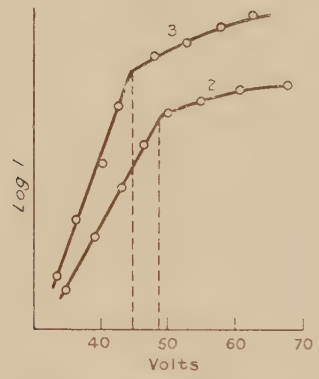
anode was a ring of nickel wire. Measurements of the potential with the fixed electrodes were made in five positions at varying intervals along the tube.

Of particular interest were the values of the potential near the filament and toward the extremity of the glow. Fig. 2 shows the electrode current plotted logarithmically, according to the method of Langmuir, for two points inside the glow, and fig. 3 shows typical curves for a point in the extreme edge of the glow. The results indicated a sharp rise of potential near the filament similar to that on the anode side of the filament, then a slightly decreasing but nearly constant potential along the glow to the farther edge, where the drop in potential was rapid. The unmistakable bend-points in the curves indicate the applicability of the Langmuir method in the present instance.

In fig. 4 the volt-ampere characteristics of the exploring electrode are shown for three successive points in the glow. Outside of the glow the branch of the curve for negative

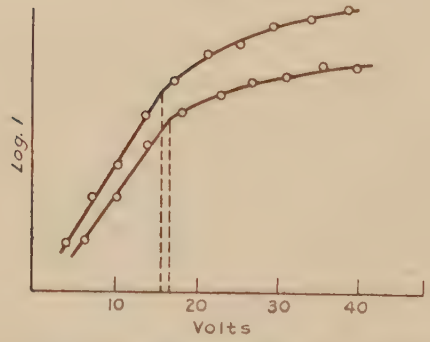
potentials (*i. e.*, positive ion current) became inappreciable, indicating that though there was a plentiful supply of positive ions in the glow there were few if any outside, although negatives were plentiful outside. From this it would appear that the glow is not due only to resonance of neutral molecules. As is well known, the necessary

Fig. 2.



Electrode potentials in glow.

Fig. 3.

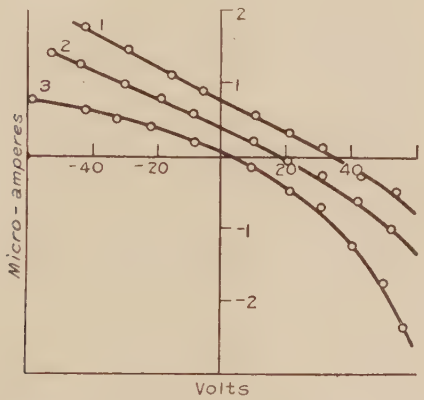


Electrode potentials in extreme edge of glow.

condition for the maintenance of an arc discharge is a sufficient density of positive ions to give the necessary positive space-charge near the cathode, by which means the requisite positive ion bombardment and cathode drop are maintained. Some information on this point was obtained by striking an arc between a second filament and plate placed in the tube, so that they were illuminated

directly by the glow from the first filament and plate. Under such conditions arcs could always be struck at potentials equal to the least potential at which the arc could normally be maintained because of the abundance of positive ions in the glow of the first arc. Just outside the glow, where electrons were still numerous, it was not possible to do this. If excited molecules were present in any abundance they were scarcely subject to cumulative action, or lower voltages would have resulted. Positive ions unquestionably were plentiful.

Fig. 4.



Volt-ampere characteristics of exploring electrode.

It has been noted by McCurdy * from the equation for the electron current to the cold exploring electrode when the velocity distribution is Maxwellian that

$$V = \frac{3}{2 \tan \theta},$$

where V is the average energy of the electrons in volts and θ is the angle of inclination of the lower portion of the curve. A consideration of fig. 3, again, shows that the slope of the curve representing a higher potential (nearer the filament) would indicate greater electron energy providing the ratio of positives to negatives did not change appreciably. Actually, however, the number of positives must decrease from the filament to the edge of the glow, where it becomes negligible. The points of zero current

* Phil. Mag. xlviii. (1924).

for the volt-ampere characteristic curves in each instance indicate that the potential of zero current was lower than the potential of the surrounding space, and decreased with increasing distance from the filament for the points measured, in the order indicated on the diagram. Hence the exploring electrode was surrounded by a positive ion space charge-sheath, which was less effective with increasing distance from the filament in keeping electrons from reaching the electrode. This resulted in a decrease in the potential of zero current as represented, and if electron energies did not increase with increasing distance from the filament, certainly the ratio of electrons to positives did increase.

Potentials up to eighty volts were applied to the anode. At high filament temperatures a two volt variation of the anode potential would at times produce as much as a ten cm. variation in the length of the glow. With lower filament temperatures, at which the glow was more diffuse and its edges less sharply defined, the reverse was true, and comparatively large variations in the potential produced only a small variation in the extent of the glow. The latter is presumably the effect mentioned by Richardson and Tanaka.

The steep potential gradient behind the filament indicates that electrons not pulled toward the anode would be accelerated in the reverse direction, producing both excitation and ionization. Beyond a certain limiting distance inelastic collisions would reduce the electron energy below that necessary to maintain the glow. Weakness of the Balmer lines indicated dissociation was slight at the lower voltages.

In conclusion, the space potential rose sharply behind the filament to nearly the value of the anode potential and dropped again sharply at the extremity of the glow. Electrons accelerated into this region would produce ionization and excitation, and at the higher potentials would seem to be more responsible for the glow than excitation by radiation. The abundance of positive ions in the glow supports the view. At lower potentials positive ions were still present, but ionization was less intense in proportion to excitation, and hence the glow was less affected by changes of potential.

Mr. Wesley Stein of North Central College made a number of the measurements.

XX. *The Specific Heat of Mercury in the Neighbourhood of the Melting-Point.* *By* L. G. Carpenter, *B.A., B.Sc.*, *and* L. G. Stoodley, *B.Sc.*, *University College, Southampton* *.

Introduction.

If a monatomic solid be considered at a temperature so high that the variation of its energy content with temperature may be calculated from classical mechanics, C_v, its atomic heat at constant volume, should be 3R. It is assumed that each atom may be considered as an harmonic oscillator, its energy being expressible in terms of the squares of its positional and momentum coordinates.

As a matter of fact at high temperatures many (presumably) monatomic solids show values of C_v which exceed 3R. The cause of this excess has been the subject of some speculation. It has been suggested that the excess is due to the variation of the energy of free electrons with temperature, to the variation of rotational energy of atoms with temperature, to premature melting caused by the presence of impurities which lower the melting-point, or to the fact that at high temperatures, when the amplitude of atomic oscillation is large, the oscillations are no longer harmonic.

The object of the work described in this paper was to obtain additional knowledge of C_v for mercury of a high degree of purity at temperatures slightly below the melting-point (where but few observations had been made). The results obtained experimentally are, of course, values of C_p, the atomic heat at constant pressure. The results have therefore been corrected to obtain C_v, although, as a matter of fact, the exact value of this correction is doubtful, mainly owing to a lack of accurate data on the expansion coefficient of solid mercury.

Apparatus and Method of Experiment.

The apparatus employed was of the well-known Nernst type, and does not call for any very detailed description. The calorimeter itself consisted of a hollow cylinder of length 8 cm., diameter 4·5 cm., and wall-thickness about $\frac{1}{4}$ mm., which was turned out of a solid piece of mild steel.

* Communicated by the Authors.

The top of the calorimeter was closed by a thin screw-on lid, in the centre of which was a hole which took a thin hollow steel tube of length 6 cm., and internal diameter 7 mm. This tube was closed at the bottom, and had a flange at the top which was hard-soldered to the lid. Thus, when the lid of the calorimeter was screwed on, there was a central cylindrical cavity, open at the top and leading into the calorimeter to a depth of 6 cm. The capacity of the calorimeter was about 95 c.c. and the weight of the steel 41·56 gms. In order to protect the mercury from possible contamination by the steel, a thin hard coat of bakelite varnish was applied to the inside of the calorimeter. The calorimeter (which was covered with a case of thin silver foil) was suspended by silk threads inside a pyrex-tube, which could be highly exhausted by means of a mercury vapour pump. Interchange of heat by radiation between the calorimeter and its surroundings was minimized by highly polished silver radiation shields. The pyrex-tube was immersed in a bath of methylated spirit, cooled with liquid air, and contained in a large Dewar vessel. The bath was vigorously stirred by means of a mechanical stirrer. Energy was supplied to the calorimeter electrically by means of a platinum coil which also served as a platinum thermometer, the measurement of energy input being made by means of carefully calibrated ammeter and voltmeter, and the resistance of the platinum thermometer measured by a Callendar-Griffith bridge. The platinum coil, which played the double rôle of heating coil and resistance thermometer, was wound non-inductively on a former of copper foil, 4 mm. in diameter, insulated by silk and bakelite varnish, and inserted in the central cavity. Thermal contact with the walls of the central steel tube was obtained by using the eutectic alloy of bismuth and lead (which melts at 125° C.) as a cement, the alloy being poured in when molten.

The platinum coil was connected by means of copper leads of 44 S.W.G., each 4 cm. in length, to stout copper wires of 22 S.W.G., which passed out of the pyrex-vessel and led to the Callendar-Griffith bridge. The considerations which determined the gauge and length of the copper leads and platinum coil were as follows :—

The leads had to be of such length and diameter that the heat-leak from the calorimeter due to their presence was not greater than a specified magnitude. On the other

hand, the electrical resistance of the leads had to be such that the heat generated in them, while energy was being supplied electrically to the calorimeter, should be small compared with the heat generated in the calorimeter coil itself. Lastly, the resistance of the platinum coil had to be such that it was measurable with the bridge available, at the highest temperature (*i.e.*, resistance) at which the calorimeter was to be used. Considerations of heat-leakage settled the leads as being 4 cm. long and of 44 S.W.G. copper, as mentioned above. This value of lead resistance necessitated a coil resistance of at least that corresponding to 1 metre of 44 S.W.G. platinum. As, however, the resistance of 1 metre of 44 S.W.G. platinum at 100° C., which was the temperature of the steam-point calibration, was too great to be measured with the Callendar-Griffith Bridge available, this resistance was partly compensated by winding 60 cm. of similar wire on the same former, and connecting this coil in the compensating side of the bridge. As a result, the resistance of the thermometer coil used as a heating coil was still that due to 1 metre of 44 S.W.G. platinum, while its effective resistance as a thermometer was that due to 40 cm. of wire. This corresponded to 11 ohms at 100° C., and was measurable with the bridge available. The calorimeter, considered as a platinum thermometer, was calibrated at the steam-point, the ice-point, and at the melting-point of mercury, and the usual Callendar formula for the platinum thermometer employed. Below − 40° C., however, the platinum scale requires correction. This was done, using the results of Van Dusen* and of Loomis†, who have investigated the platinum thermometer at low temperatures. The heat capacity of the calorimeter, when filled with mercury, was determined in the usual manner, the rise of temperature due to a measured amount of electrical energy being determined by resistance measurements, correction being made for the slight loss of heat which occurs during the input period.

When measuring the heat capacity of the mercury and calorimeter over the range −90° C. to −40° C., the time of heat input was usually 4 minutes, the current being about 300 milliamps, and the voltage about 4·5 volts. The resulting temperature rise was of the order of $1\frac{1}{2}$° C. In order to calculate the specific heat of the mercury it

* Am. Chem. Soc. Journ. xlvii. p. 326 (1925).
† Am. Chem. Soc. Journ. xlvii. p. 851 (1925).

was of course necessary to know the heat capacity of the calorimeter alone. To this end a separate set of experiments was carried out to determine the specific heat of the steel, which contributed about 80 per cent. of the total heat capacity of the calorimeter. the specific heats of the small quantities of platinum, silver foil, solder, etc., used in its construction being taken from tables. Over the range of temperatures covered in this research the heat capacity of the calorimeter was 12 per cent. of the heat capacity of the mercury it contained.

Purification of the Mercury.

It has already been stated that a possible explanation of the increase of C_v above 3R near the melting-point is to attribute it to the presence of impurities, which lower the melting-point, so that some fusion takes place below the melting-point of the pure substance. Thus, the apparent rise of the specific heat would be due in reality to the effect of latent heat of fusion. Such an effect has, in fact, been observed by Dickinson and Osborne * in some precision experiments made by them on the specific heat of ice.

In the present research, therefore, it was resolved to use mercury of a high degree of purity, and, further, to compare the results with those obtained with mercury of a less degree of purity. The two samples of mercury used were called the P and D samples respectively. In order to obtain the P sample of mercury the following procedure was adopted.

A quantity of mercury was taken from a laboratory stock which had been passed in the form of a fine spray five times through 20 per cent. nitric acid, and, after washing with water, distilled once *in vacuo*. The mercury was then agitated with a 2 per cent. solution of potassium cyanide by sucking air through the mixture, small quantities of sodium peroxide being added twice a day. This removed the bulk of any noble metals present †. After washing, the mercury was shaken well with a mixture consisting of equal volumes of 9N sulphuric acid and a cold-saturated solution of potassium permanganate. Shaking was continued until the pink colour disappeared,

* Bureau of Standards, Bull. xii. p. 49 (1915).
† Bettel, Chem. News, xcvii. p. 158 (1908).

the solution then being renewed. This method also is said to remove any base metals present *. After renewing the solution about ten times the mercury was separated from the white precipitate which had formed, and was washed, dried, and filtered through a pinhole. It was then subjected to two distillations in a current of air under a reduced pressure of 30 millimetres, in order to remove final traces of the base metals, and to eliminate the noble metals. Hulett † states that, starting with a saturated solution of silver, not more than 0·03 parts in a million remain after two such distillations.

After the experiments were finished the P sample was taken from the calorimeter and sent to Messrs. Adam Hilger for a spectroscopic examination. Their report was as follows :—" Antimony, iron, magnesium, calcium, and silicon—a trace. Zinc, cadmium, arsenic, bismuth, lead, silver, boron, and carbon were specially sought, with negative results. A minute trace of tin may have been present, but the indication was so faint as not to be conclusive."

The D sample was taken from the laboratory stock mentioned above, and was used without further purification. Its treatment, therefore, consisted in having been passed five times through 20 per cent. nitric acid, washed, and then distilled *in vacuo*.

The Experimental Results.

Previous determinations of the specific heat of mercury have been made by Koref ‡, Pollitzer §, Simon ‖, Russell ¶, and Barnes and Cooke **. In Table I. are given the values of Cp obtained by the present authors; the range of temperature is from 197·6° abs. to 285·15° abs. In fig. 1 have been plotted our results for the P sample of mercury in a graph which extends from 190° to 250° abs., together with such results of Koref, Pollitzer, and Simon as lie in this range. It is not convenient to plot, on a single graph,

* Russell, Evans, and Rowell, Chem. Soc. Journ. cxxviii. p. 1872 (1926).
† Phys. Rev. xxxiii. p. 307 (1911).
‡ *Ann. d. Physik*, xxxix. p. 49 (1911).
§ *Zeits. Elektrochem.* xix. p. 513 (1913).
‖ *Ann. d. Physik*, lxviii. 3, p. 241 (1922).
¶ *Phys. Zeits.* xiii. p. 59 (1912).
** Phys. Rev. xvi. p. 65 (1903).

our results together with all the results of other observers, as, on the rather small scale which would have to be used, the points would be too crowded. On fig. 1. therefore, a curve has been drawn which best represents our results from the lowest temperature at which we worked (197°·6

Table I.

Absolute Temperature.	Atomic Heat (at constant pressure).
197·6	6·41
199·4	6·495
201·1	6·50
207·5	6·495
208·05	6·515
208·6	6·59
209·9	6·55
212·9	6·505
214·45	6·515
217·6	6·60
218·9	6·68
222·9	6·65
227·4	6·72
229·2	6·79
229·65	6·755
231·0	6·755
231·0	6·74
232·4	6·738
232·7	6·785
233·8	6·755
234·23	Melting-point
236·5	6·80
285·15	6·70

abs.) to the melting-point (234°·2 abs.). On fig. 2. which extends from 100° to 300° abs., the curve so obtained has been plotted, together with the results of all other observers who made determinations in this range. A curve which best represents our results from the melting-point to 300° abs. has been drawn, and the points obtained for the

Fig. 1.

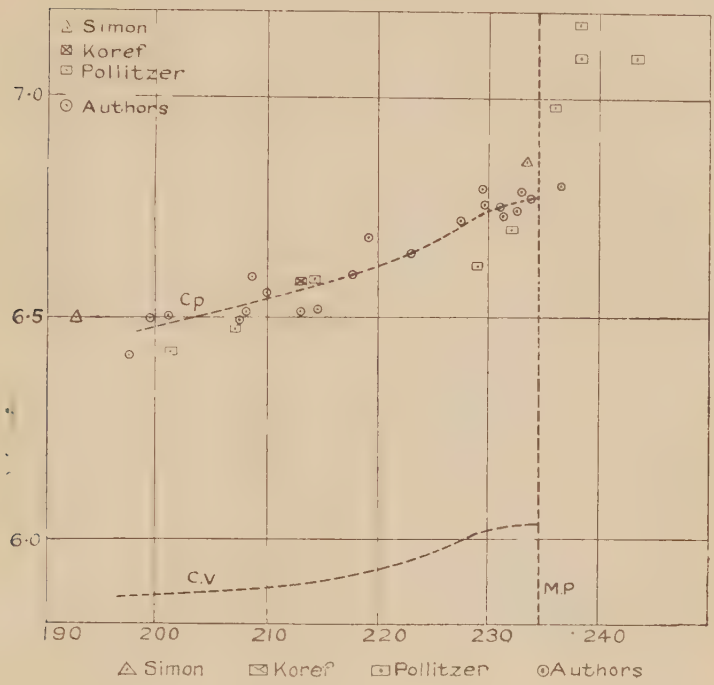
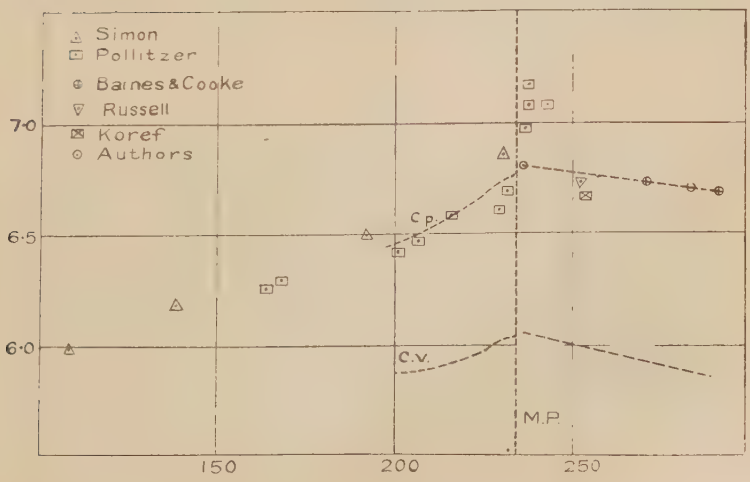

Simon
Koref
Pollitzer
Authors
7·0
6·5
6·0
Cp
C.V
M.P
190
200
210
220
230
240
Simon
Koref
Pollitzer
Authors

Fig. 2.


Simon
Pollitzer
Baines & Cooke
Russell
Koref
Authors
7·0
6·5
6·0
Cp.
C.V.
M.P.
150
200
250

liquid by Russell, Koref, Pollitzer, and by Barnes and Cooke have been plotted for comparison.

It is particularly satisfactory to notice that the line joining our two values for the liquid at 236°·5 abs. and 285°·15 abs. agrees very closely indeed with the line joining the two points for the liquid obtained by Barnes and Cooke, whose work was of a very high order of accuracy. Hence we feel confident that no serious systematic error is to be found in our own work. We estimate that our experimental arrangements were such as to give the true value of C_p within 1 per cent. This estimate is confirmed by the fact that on fig. 1, on which all our results for the solid have been plotted, the greatest divergence of points from the average curve we have drawn is 1 per cent., while the average deviation is considerably less. The values of C_p have, as a matter of fact, been computed to about 1 part in 700 in Table I., but an experimental accuracy of this order is not claimed. As to the results for the D sample, they were identical with those for the P sample within the limits of experimental accuracy. At the melting-point itself, indeed, the values obtained for the P and D samples were the same within two parts in 700, but, of course, the closeness of this agreement was probably partly accidental.

The $C_p - C_v$ *Correction.*

The difference between the specific heats at constant pressure and at constant volume is given (in mechanical units) by the expression

$$C_p - C_v = \frac{\alpha^2 V T}{\kappa},$$

where α is the coefficient of cubical expansion, V is the molecular volume, T the absolute temperature, and κ the compressibility. For mercury in the liquid state the values of α and κ have been determined with considerable accuracy by Bridgman *. The value of V, the molecular volume, at each temperature T is also known with sufficient accuracy for our purpose. Values of $C_p - C_v$ for various temperatures of liquid mercury have therefore been calculated from Bridgman's data, and by subtraction from the C_p curve the C_v curve has been obtained, and plotted

* Am. Acad. Proc. xlvii. p. 347 (1911).

on fig. 2. The situation with regard to solid mercury is much less satisfactory. The compressibility is indeed known from Bridgman's work, being about $3{\cdot}37 \times 10^{-6}$ cm.^{2}/kgm., but there is considerable uncertainty as to the expansion coefficient. According to Dewar * the coefficient of cubical expansion of mercury over the range from $-188°{\cdot}7$ C. up to the melting-point is $0{\cdot}887 \times 10^{-4}$, while Grunmach † gives $1{\cdot}23 \times 10^{-4}$ for the same coefficient over the range $-80°$C. to the melting-point.

As Bridgman remarks (*loc. cit.*) Grunmach used a dilatometer method in which he made no correction for the effect of the glass envelope, and the value he obtained by this method for the change of volume on freezing is certainly wrong. Bridgman himself gives a value of $1{\cdot}45 \times 10^{-4}$ (which is the mean of two determinations 1·25 and $1{\cdot}65 \times 10^{-4}$) for the region just below the melting-point, which value, though extremely rough, he considers is probably as good as that of either Dewar or Grunmach. The empirical correction $C_p - C_v = aT^{\frac{3}{2}}$ has been employed by Pollitzer ‡ and by Simon ‡ for mercury, with $a = 21 \times 10^{-5}$. This formula gives $C_p - C_v = 0{\cdot}753$ calorie per gram atom at the melting-point. Assuming that this value is actually correct, and taking Bridgman's value for the compressibility of the solid, viz., $3{\cdot}37 \times 10^{-6}$ cm.^{2}/kgm., the coefficient of cubical expansion would be $1{\cdot}8 \times 10^{-4}$. This is higher than the values of either Dewar, Grunmach, or Bridgman, and is equal to the value for the liquid immediately above the melting-point. It is therefore almost certainly too high, since the expansion coefficient of an element immediately above the melting-point is probably always greater than the coefficient of expansion immediately below the melting-point. For the only three elements for which data is to be found in the Landolt-Börnstein's tables, viz., phosphorus, sodium, and potassium, the expansion coefficients of the liquid phase are greater than those of the solid phase by about 34 per cent., 13 per cent., and 17 per cent. respectively. Thus the expansion coefficient of solid mercury at the melting-point may be taken as less than $1{\cdot}8 \times 10^{-4}$, and the $C_p - C_v$ correction is therefore less than 0·753 at this temperature.

* Roy. Soc. Proc. lxx. p. 237 (1902).
† *Phys. Zeits.* iii. p. 133 (1902.)
‡ *Loc. cit.*

As, however, the real value is not known, the correction has been calculated from $C_v - C_r = 21 \times 10^{-5} T^2$, and the C_v curve inserted on figs. 1 and 2. Nevertheless, we emphasize the fact that 6·02, the value of C_v at the melting-point shown on the curves, is almost certainly too low. A more accurate determination of the expansion coefficient of solid mercury is obviously highly desirable, and is being carried out in this laboratory.

In order that the values obtained from our smoothed curves may be readily available to anyone who may be interested in the exact numerical values which we consider

Table II.

Absolute Temperature.	C_p.	C_v.
200 solid	6·47	5·875
210 „	6·54	5·90
220 „	6·62	5·93
225 „	6·68	5·97
230 „	6·75	6·01
234 „	6·77	6·02
240 liquid	6·79	6·04
250 „	6·76	6·00
260 „	6·74	5·96
270 „	6·72	5·93
280 „	6·70	5·88
290 „	6·68	5·82

most probable, they are set out in Table II. It should be remembered that, while the exact value of C_v for the solid is doubtful on account of the uncertain $C_v - C_r$ correction, the value of C_v for the liquid is much more reliable, since it depends only on our measurements (which are in good agreement with those of Russell * and Barnes and Cooke *) and on the direct and trustworthy determinations of α and κ by Bridgman.

Discussion of Results.

In this section of the paper we will discuss the validity of the experimental results obtained, so as to provide a

* *Loc. cit.*

foundation of fact for whatever theoretical speculation may subsequently be possible.

The purity of the mercury may first be considered. Messrs. Adam Hilger's analysis, though not quantitative, may be taken as showing that the amount of impurity in our P sample was certainly small. The specific heats obtained with the D sample were, however, the same as those obtained with the P sample. Assuming that the additional treatment of the P sample resulted in a higher degree of purity, there are two possible explanations :—

1. The mercury was so pure that the effect of any residual impurity was not detectable with our apparatus. In this case the slope of our curve is not due to impurity.
2. The P sample was fairly pure, and the D sample much less so, but the effect of the impurity remains constant until practically the last trace has disappeared. In this case the slope of our curve is due to impurity.

Alternative 2 seems definitely much less probable than alternative 1. We therefore conclude that the shape of the curve near the melting-point is not due to impurity.

It has been found by some observers (*e.g.*, Griffiths *—in the case of sodium) that the specific heat of a metal depends on the previous heat treatment of the specimen. In the case of the present experiments the points on the curve were obtained on several different days, the mercury being allowed to melt between one set of observations and the next. The temperature ranges of the various sets of observations overlapped, but no systematic difference was found between the observations obtained on different days, although the time of freezing and amount of cooling were varied. Hence it is not probable that the results were vitiated by want of annealing.

Comparing our results with those of other observers, it is evident from fig. 1 that our C_p curve lies between those of Simon and Pollitzer, being about 1 per cent. lower than the former, and 1 per cent. higher than the latter,and agrees closely with Koref's value for 213·6° abs., which, however, is a mean atomic heat over the range from 195·9° to 231·3° abs. Since only two observations of Simon lie within the

* Roy. Soc. Proc. lxxxix. p. 561 (1914).

temperature range of the present experiments, it is not possible to deduce what slope he would ascribe to the curve in the immediate neighbourhood of the melting-point. Pollitzer's results, on the other hand, show a sudden and steep rise about 4° below the melting-point. In view, however, of the fact that he made only two determinations in the neighbourhood of the melting-point, and of the rather erratic nature of his results, no great weight need be attached to it. It can therefore fairly be said that the results of the present experiments are in good general agreement with those of other observers, and give considerably more detailed information as to the shape of the specific-heat curve in the immediate neighbourhood of the melting-point.

The value of C_p measured at the melting-point is 6·77; if we subtract the $C_p - C_v$ correction of $21 \times 10^{-5} T$ used by Pollitzer, the corresponding value of C_v is 6·02. It has already been pointed out, however, that this value of $C_p - C_v$ is almost certainly too high, since it involves assuming a value of the expansion coefficient for the solid as large as that for the liquid. Hence, at the melting-point, C_v is at least equal to 6·02, and in all probability is higher*. It seems therefore that at the melting point C_v exceeds the value of 5·95.

It is evident from our measurements that above about 210° abs. the slope of the curve begins to increase, although Debye's equation would lead one to expect it to become more nearly parallel to the axis of temperature and asymptotic to 5·95. It might, perhaps, be argued that this increase of C_p is only apparent, and is in fact due to an unexpected increase of $C_p - C_v$ in this region, caused by increase of α or decrease of κ or both. This view, however, is hardly tenable. It is unlikely that α suddenly increases in the neighbourhood of the melting-point, and in the case of sodium, where such an effect has been specially sought†, it has been found to be absent. κ, on the other hand, may be expected to increase rather than decrease as the melting-point is approached. This is shown, for example, by some

* A rough estimate of how much higher can be made if we assume the expansion coefficient of the solid to be of the order of 10 per cent. less than that of the liquid—which seems a reasonable assumption to make in view of the values in the case of sodium, potassium, and phosphorus. This would reduce $C_p - C_v$ by about 20 per cent. and increase the value of C_v at the melting-point to about 6·17.

† Griffiths, Phys. Soc. Proc. xxvii. p. 477 (1915).

measurements on tungsten made by Geiss, and quoted by Zwikker *.

The specific-heat curve becomes nearly parallel to the axis of temperature in the immediate neighbourhood of the melting-point. Of the reliability of the experimental evidence on this point there can be no doubt. As has already been stated, the results for the D sample of mercury were identical with those of the P sample within the limits of experimental accuracy: further, a preliminary set of determinations was made with the P sample, in which a variable source of error (which was subsequently determined and eradicated) made the results rather erratic. Nevertheless, the mean curve given by these preliminary determinations also became horizontal in the immediate neighbourhood of the melting-point. In fact, it was substantially identical with the curve recorded in this paper.

It may therefore be concluded that the curve representing the specific heat of mercury as a function of temperature in the neighbourhood of the melting-point exceeds the value that would be expected on the basis of an extrapolation from the value at lower temperatures made in accordance with Debye's theory. Further, the value of C_v at the melting-point in all probability exceeds 5·95; and, finally, the curve in the immediate neighbourhood of the melting-point is not concave upwards, but becomes more nearly parallel to the axis of temperature as the melting-point is approached.

Some Theoretical Considerations.

The excess of the atomic heat of metals above 3R at high temperatures has been treated by several writers. So far as we are aware, the effect has been observed up to the present only in the case of metallic elements. It is true that White † has argued that the phenomenon is a general one, and is not confined to metals. He supports this view by quoting measurements he made on certain silicates, for which C_v departs from Debye's curve at high temperatures. As, however, in no pure silicate on which he experimented did C_v actually exceed 5·95, his thesis requires to be supported by further evidence.

The fact that in metals C_v exceeds 3R at high temperatures has generally been explained in terms of one of two

* *Zeits. f Physik*, liii. 9–10, p. 668 (1928).

† Nat. Acad. Sci. Proc. iv. p. 343 (1918).

hypotheses, of which the first is that it is attributable to anharmonic oscillations of atoms, and the second is that it is the result of the participation of the free electrons in the thermal energy of the atomic lattice. The first hypothesis has been enunciated by Lindemann* in a paper in which (having shown that Honda's † theory, which attributes the effect to atomic rotations in the solid state, is untenable) he remarks that a simple application of Taylor's Theorem shows that the restoring force on a displaced atom in the lattice is elastic for small displacements, but does not remain so for large displacements. Hence the mean potential energy equals the mean kinetic energy at low temperatures, but may exceed it near the melting-point. It is evident that, if the average potential energy of oscillations of the atoms in a gram atom of metal is to exceed the average kinetic energy (*i.e.*, exceed $\frac{3}{2}$ R.T.), the restoring force on a displaced atom must increase more slowly than in a linear proportion to the displacement. The dependence of the average potential energy on the relation between restoring force and displacement has been treated by Tolman ‡, who shows, for instance, that if the restoring force varies as the nth power of the displacement, then the average potential energy of an oscillator will be $\frac{kT}{n+1}$ per degree of freedom, giving, of course, the familiar $\frac{k}{2}$T per degree of freedom for the simple harmonic oscillator. Braunbek §, also, has made use of the conception of anharmonic oscillations near the melting-point to explain the anomalous increase of C_v: while Waller ‖, considering the case of a one-dimensional lattice, has worked out the conditions under which the atomic heat at constant volume of such a lattice should exceed R.

The specific heat of a solid consisting of anharmonic oscillators has also been treated by Born and Brody ¶, in accordance with the quantum theory, but Schrödinger ** has shown that their results can equally well be obtained by the use of classical mechanics.

* Phil. Mag. xlv. p. 1119 (1923).
† Phil. Mag. xlv. p. 189 (1923).
‡ 'Statistical Mechanics,' p. 76 (Chemical Catalog. Co., 1927).
§ *Zeits. f. Physik*, xxxviii. 6–7, p. 549 (1926).
‖ *Ann. d. Physik*, lxxxiii. 2, p. 153 (1927).
¶ *Zeits. f. Physik*, vi. 2, p. 132 (1921).
** *Zeits. f. Physik*, xi. 3, p. 170 (1922).

Turning now to the second hypothesis, viz., that the effect is due to the participation of free electrons in the thermal energy of the atomic lattice, we find that a considerable use has been made of it by Eastman * and others in America. These investigators have examined the excess of C_v over 3R for a large number of metals, and claim that it is the greater the more electro-positive the metal. This correlation is, however, not very well marked, and Eastman †, indeed, admits that the hypothesis of anharmonic oscillations is particularly well suited to explain the relatively rapid increase of specific heat which is found in some substances in the immediate neighbourhood of the melting-point, but he considers that the effect of the free electrons is also present over the whole range of high temperatures. Now, Sommerfeld ‡ has recently estimated, by the aid of Fermi-Dirac statistics, the contribution which free electrons should make to the specific heat, if one free electron per atom is assumed. He arrives at the result

$$(C_v)_{\text{electrons}} = \pi^2 \frac{nk}{h^2} \left(\frac{8\pi}{3n}\right)^{\frac{2}{3}} \mathrm{RT},$$

in which m is the mass of an electron, k is Boltzmann's constant, h Planck's constant, and n is the number of free electrons per cubic centimetre, which is assumed to be equal to the number of atoms per cubic centimetre. The free electrons are treated as a gas, and their interaction with the atomic cores of the lattice is neglected. The application of this formula to solid mercury at its melting-point gives

$$(C_v)_{\text{electrons}} = 0{\cdot}04 \text{ cals./gram. mol./deg.}$$

If this is subtracted from our value of C_v at the melting-point, viz., 6·02 (which is, as we have already emphasized, a lower limit), the contribution of atomic oscillations to C_v would be 5·98, a value which is, of course, to our order of accuracy, experimentally indistinguishable from the limiting value of Debye's theory, 5·95. Although Sommerfeld's theory, which perhaps cannot be expected to yield more than order of magnitude, might possibly suffice to explain our value of C_v at the melting-point, without having recourse to the hypothesis of anharmonic oscillations, yet,

* Am. Chem. Soc. Journ. xlvi. p. 1184 (1924).
† *Loc. cit.*
‡ *Zeits. f. Physik,* xlvii. 1–2, p. 1 (1928).

as it stands, it does not explain the shape of the C_v curve, in particular the rise at about 210° abs., and the subsequent tendency at the melting-point to parallelism with the axis of temperature.

The explanation, if it is to be found solely in terms of electrons, is no doubt connected with the interaction of the electrons with the atomic cores, which has been taken into account by Bloch *. If the interaction of the increasingly disordered lattice with the electrons is the cause of the observed phenomena, it seems that such an effect must also be present in the liquid state. Whether the anomalous rise of C_v is due to anharmonic vibrations or to the effect of electrons, or to both these causes acting together, it is clear that it must be associated with large atomic vibrations and with atomic disorder, since these phenomena are characteristic of an approach to the melting-point. It is well known that at higher temperatures atomic oscillations are to some extent anharmonic, and, indeed, as Debye has pointed out, if it were not so, the coefficient of expansion of solids would be zero. Having granted, then, that near the melting-point atoms will depart from simple harmonic motion, it is difficult to resist the conclusion that such departure will affect the specific heat. The exact extent of this contribution cannot at present be determined, but, in our opinion, it certainly exists.

Investigations on other substances are in progress in this laboratory in order to elucidate the matter.

Summary.

Observations of the specific heat of pure mercury have been made over a range of 200° to 285° abs., which includes the melting-point (234° abs.). The results have been reduced to give values of C_v, the atomic heat at constant volume, though, owing to lack of accurate data on the expansion coefficient, the reduction is somewhat doubtful.

The shape of the C_v curve is significant in that it shows an increase of slope in the neighbourhood of 210° abs., followed by a subsequent flattening. The curve is certainly not concave upwards at the melting-point.

The significance of the results obtained is discussed with regard to the relative contributions of free electrons and of anharmonic atomic oscillations.

* *Zeits. f. Physik*, lii. 7/8, p. 555 (1928).

Our thanks are due to Professor Lindemann, who suggested this investigation, to Professor Stansfield, in whose laboratory it was carried out, and to the Department of Scientific and Industrial Research, who made it possible for one of us (L. G. Stoodley) to engage in the work.

16th April, 1930.

XXI. *The Dielectric Polarization of Liquid Mixtures and Association.*—Part I.

By N. N. Pal, *M.Sc., Research Scholar, Dacca University* *.

Abstract.

The paper describes an investigation, by the heterodyne heat method, of the dielectric polarization of mixtures of nitrobenzene and benzene and of nitrobenzene and carbon tetrachloride, of various concentrations and at various temperatures. The results are discussed on the basis of Debye's dipole theory and the assumption of molecular association.

Introduction.

It is well known that the Debye expression for the dielectric constant of a medium consisting of electrically polar molecules fails in the case of liquids, though the agreement is generally very good in the case of vapours.

We explain this failure on the assumption that in the liquid state the polar molecules do not all exist in the same simple form, but that a considerable fraction of the total number combine to form more complicated structures. We have independent experimental evidence in favour of this existence of association, and one would generally expect that the molecules with large electrical moment would naturally show this tendency to associate to a marked degree.

The nature of this association is, however, not very clearly understood; Debye † has suggested an electrical theory of association, much on the same lines as his theory of dissociation, and has shown that the general qualitative nature of the phenomena can in some cases be explained from this standpoint. It is clear, however, that more data regarding the

* Communicated by Prof. S. N. Bose, M.Sc.

† Debye in Marx's 'Handbuch der Radiologie,' vi. (1925).

various influences of dilution and temperature on the so-called association have to be collected and compared with the theory before it can be regarded as satisfactorily established. The measurements of dielectric constants of binary mixtures, consisting of a polar and a non-polar liquid, may be expected to give valuable data regarding the nature of association, as we can thus vary the concentration of the polar molecules.

This aspect of the problem does not seem to have attracted much attention; most of the work done on the dielectric constants of polar liquids (except those of Lange* and Williams and Mathews†) have been with a view to determine the permanent electric moment of the individual molecules, and for this purpose the general tendency has been to concentrate on the values of the dielectric constants of mixtures at large dilutions rather than a careful determination of the general behaviour.

It is with an aim to examine more closely the nature of the association that this work has been taken up. The programme of work has been to take mixtures of different non-polar solvents and to examine carefully the influence of temperature and concentration, as well as the action of the solvent in each case.

The present paper, which forms Part I. of the series, describes a detailed study of the dielectric polarization of nitrobenzene in solutions of carbon tetrachloride and benzene at different concentrations and at various temperatures, and an attempt is made to correlate the general features of the results obtained with the electrical theory of association.

Experimental Procedure.

The measurements of dielectric constants were made by a heterodyne beat arrangement similar to that used by Zahn‡ in the case of gases. The general arrangement of the apparatus will be clear from fig. 1. As this method of measurement is now sufficiently well known, we need mention here only those points which are specially important in this connexion.

As pointed out by Zahn, the accurate determination of the dielectric constants mainly depends upon a careful calibration of the condenser system. Great importance has, therefore, been attached to the calibration of the condenser system, which consists of the variable condenser 500 m.m.F., a

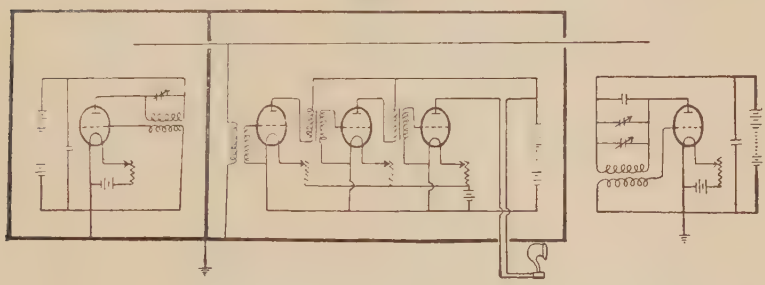
* Lange, *Zeits. f. Phys.* Bd. 33 (1925).
† Williams and Mathews, *Zeits. Phys. Chem.* cxxx. (1927).
‡ C. T. Zahn, Phys. Rev. xxiv. (1920).

vernier condenser 25 m.m.F., and the cell condenser, all placed in parallel. One division of the scale attached to the variable condenser corresponds to $\frac{1}{2}$ m.m. F., while that of the vernier one reads 1/25 m.m.F. The calibration of the bigger condenser has been carefully made by a fixed air condenser specially prepared for the purpose, and that of the vernier one by a neutrodyne condenser. Every condenser was carefully shielded, and final adjustments of the condenser were made from a distance by means of a long glass rod. In fact, the method was very sensitive for the present purpose.

The measurements were done by electric waves of 1200 kilocycles. Marconi P.M. 4 valves were used to produce the continuous oscillations, while Cossor valves were employed in the amplifying circuit.

The cell condenser is a cylindrical gold-plated brass condenser with about 1·5 mm. separation between the

Fig. 1.



cylinders and is similar to that used by Zahn. The two cylinders are held together and insulated by means of two small glass pieces (fig. 2). The condenser is mounted in a glass tube fitted up with a glass-stoppered mouth.

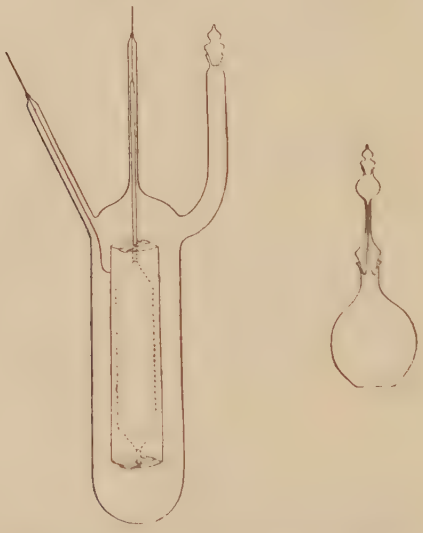
The oscillations were observed to be steady only after half-an-hour's run, as was evident from the constancy of the beat note between the fork (electrically maintained) and the loud speaker. Readings were always taken when this secondary beat note became steady, for then the cell condenser had assumed the temperature of the bath.

The capacity of the cell condenser under any circumstances was measured by the method of substitution, except when with the higher concentration of nitrobenzene its capacity was greatly increased and went outside the limit of the variable condenser. The cell capacity under these conditions was determined by measuring the effective capacity of the cell and an auxiliary fixed condenser placed in series. Of

course, the original sensitiveness is to some degree diminished, but it is recovered to a great extent by making the fixed condenser as great as the variable one. In the particular experiment one of 450 m.m.F. was used, which was carefully shielded, preserved from external heat, and calibrated in position. The cell capacity thus measured was corrected for the lead capacity, which was determined by preparing an imitation lead and measuring its capacity. The contribution from the glass pieces was calculated to be very small.

The liquids used were Merck's extra pure; they were shaken with calcium chloride, kept over night and after

Fig. 2. Fig. 3.



The cell condenser and the sp. gr. bottle.

decantation twice distilled, the distillate being received in a vessel provided with a side tube containing calcium chloride. The purpose was to obtain samples pure and free from moisture. Solutions were made by mixing known weights of two components. The process of weighing and mixing was made in stoppered flasks, so that there was evaporation only when the solution was being transferred from one vessel to another. Owing to the large capacity of the cell (100 c.c.), this, however, did not appreciably affect the concentration or the measurement.

A water bath in a large glass vessel was used, care being taken to maintain the constant level of the bath and to dip

the condenser in the bath up to the same point, for although the condenser was shielded on account of its outside cylinder being earthed, a slight effect of the level of the bath upon the capacity was noticed. The density bottle was suspended in the bath by a network of threads.

The density measurements were made simultaneously with the dielectric constant measurements in the same bath by a gravity bottle fitted up with a special type of mouth (fig. 3). The error in the density measurements seems to be not greater than 5 in 10,000.

Discussions and the Results.

According to Debye * P, the molar dielectric polarization of a perfectly miscible binary liquid mixture, is given by

$$P = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M_1C_1+M_2C_2}{\rho},$$

where ϵ and ρ are the dielectric constant and the density of the mixture. M_1, M_2 and C_1, C_2 are the molecular weights and molar fraction concentrations of the non-polar and the polar liquids respectively.

P can also be assumed as equal to $P_1C_1 + P_2C_2$, where P_1 denotes the contribution to the total polarization of the non-polar solvent, and may be put equal to

$$\frac{\epsilon_1-1}{\epsilon_1+2} \cdot \frac{M_1}{\rho_1},$$

and P_2, the polarization due to the polar solute. Since these molecules of the second kind have dipole moments, we can further split it up into two portions, first, the induced polarization A, which is generally taken to be the optical value extrapolated to zero-frequency, and a part P_3. In the absence of association, according to the simple Debye theory, P_3 can be expressed in the form $\frac{B}{T}$, where $B = \frac{4\pi}{3} \frac{N\mu^2}{3k}$, μ being the electrical moment of the molecule.

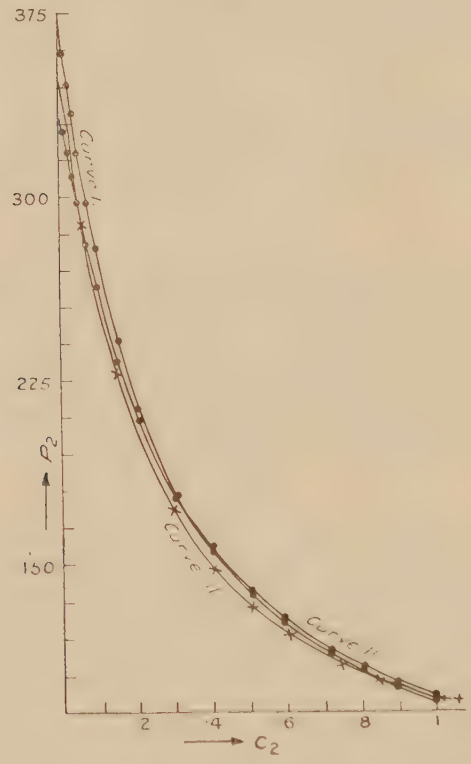
A determination of B therefore enables us to calculate the electric moment of the dipole molecule. The presence of association, on the other hand, is revealed by the variation of P_3 with concentration even at any fixed temperature.

On the assumption that the increase in dilution or the rise of temperature will favour dissociation, we can try to interpret the variation of P_3 with increasing dilution as an indication

* Debye in Marx's 'Handbuch der Radiologie,' vi. (1925).

of the presence of a greater number of unassociated molecules. In the particular case of nitrobenzene the dilution increases P_2 continuously, as will be seen in Curve I. and from Tables I. and II. (pp. 272–274), and hence we can conclude that the association tends to generate complex molecules of lesser moments.

CURVE I.



Curve I. For nitrobenzene at 10° C. with CCl_4 as solvent.
Curve II. „ at 50° C. „ „
Curve III. „ at 27° C. with benzene as solvent.

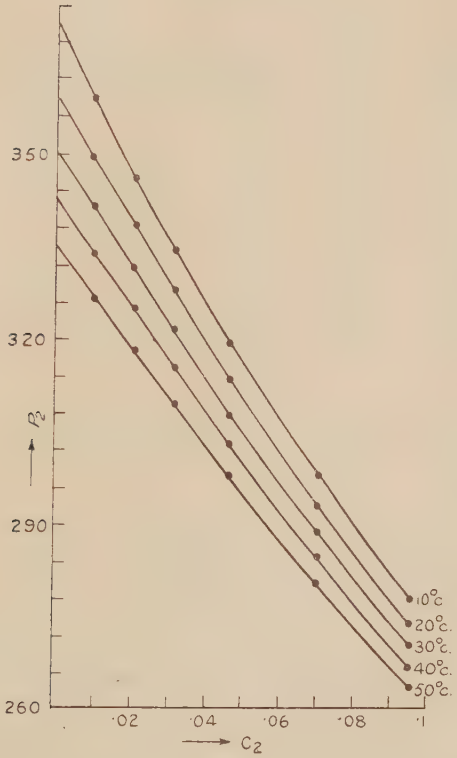
If we assume, as suggested by Debye*, that association consists in the formation of double molecules with zero moment in this particular case, which will be easily understood if we regard the molecules as having an elongated

* Debye in Marx's 'Handbuch der Radiologie,' vi. (1925).

shape, which tend to form mutually compensated pairs, we can regard the polarization P_2 as consisting of contributions from n_1 undissociated molecules and n_2, the rest, being dissociated molecules. Then P_2 can be written as

$$P_2 = n_1 A' + n_2 \left(A' + \frac{B'}{T} \right) = \tfrac{1}{k}(n_1 + n_2) A' + n_2 \frac{B'}{T}.$$

CURVE II.



Polarization curves for nitrobenzene with CCl_4 as solvent.

In the above formula, we assume that both the dissociated as well as the undissociated molecules have the same induced polarization, whereas it is only the dissociated molecules which contribute a further portion in the dielectric polarization by an orientation which evidently can be calculated and expressed in terms of the usual kinetic theory basis as in the

TABLE I.

Nitrobenzene and Benzene.

$t = 27°$ C. n, number of nitrobenzene mols. per c.c.

$$= \frac{\rho C_2}{M_1 C_1 + M_2 C_2} \cdot N.$$

C_2.	ρ.	ϵ.	P.	$n/N \times 10^4$.	P_2.	$B \times 10^{-2}$ with $A = 33$.
0	·8707	2·275	26 73	0		
·0624	·8919	3·708	42·98	6 882	287·1	762
·1475	·9243	5·811	56·39	16·11	227·8	584·4
·2984	·9806	10·064	70 03	32·0	171·8	416·4
·4088	1·019	13·55	76·38	43·20	148·1	345·3
·5105	1·052	16·92	80·74	53·19	132·5	298·5
·6132	1·085	20-56	84·35	62·99	120·7	263·1
·7478	1·126	25·60	88·37	75·43	109·2	228·6
·8437	1·155	29·70	90·90	84·01	102·8	209·4
1	1·196	33·0	94·73	97·21	94·73	185·2

TABLE II.

Nitrobenzene and Carbon Tetrachloride.

C_2.	$t°$ C	ρ_0.	ϵ_0.	P.	$n/N \times 10^4$.	P_2.	$B \times 10^{-2}$
0	10	1·6133	2·245	27·967	0		
	20	1·5940	2·224	27·966			
	30	1·5747	2·203	27·962			
	40	1·5555	2·183	27·972			
	50	1·5362	2·163	27·977			
·009851	10	1·6094	2·460	31·230	1·033	358·9	922·3
	20	1·5903	2·428	31·134	1·020	349·2	
	30	1·5712	2·398	31·061	1·008	341·7	935·4
	40	1·5520	2·368	30·982	·996	333·7	
	50	1·5328	2·339	30 910	·983	326·4	947·7
·02101	10	1·6047	2·709	34·645	2 201	345·7	884 9
	20	1·5859	2·666	34·490	2·175	338·3	
	30	1·5669	2·625	34·350	2·149	331·6	904·8
	40	1·5479	2·585	34·212	2·123	325·1	
	50	1·5289	2·546	34·075	2·097	318·5	922·2
·03193	10	1·6006	2·961	37·748	3·344	334·2	852·5
	20	1·5818	2·906	37·541	3·304	327·7	
	30	1·5628	2·853	37·344	3·265	321·5	874·2
	40	1·5438	2·802	37·154	3·225	315·6	
	50	1·5248	2·752	36·958	3·185	309·5	893·1

TABLE II. (*cont.*)

Nitrobenzene and Carbon Tetrachloride.

C_2.	$t°$ C.	n_D.	ϵ_0.	P.	$n/N\times10^4$.	P_2.	$B\times10^{-2}$.
·04686	10	1·5946	3·314	41·615	4·903	319 2	809·9
	20	1·5759	3·240	41·338	4·846	313·2	
	30	1·5571	3·170	41·078	4·788	307·7	832·3
	40	1·5383	3·106	40·860	4·730	303·0	
	50	1·5196	3·042	40·615	4·673	297·8	855·3
·07064	10	1·5849	3·900	47·034	7·382	297·8	749·4
	20	1·5665	3·796	46·703	7·296	293·2	
	30	1·5481	3·698	46·386	7·211	288·7	774·8
	40	1·5295	3·606	46·094	7·124	284·5	
	50	1·5108	3·520	45·827	7·037	280·8	800·4
·09586	10	1·5745	4·549	51·930	10·00	277·92	693·1
	20	1·5566	4·408	51·550	9·89	273·95	
	30	1·5385	4·276	51·191	9·77	270·21	718·7
	40	1·5203	4·154	50·863	9·66	266·80	
	50	1·5022	4·046	50·602	9·54	264·06	746·3
·1527	10	1·5516	6·101	60·520	15·89	241·13	589·0
	20	1·5342	5·877	60·183	15·71	238·93	
	30	1·5169	5·674	59·880	15·53	236·94	617·9
	40	1·4995	5·485	59·592	15·35	235·06	
	50	1·4823	5·313	59·335	15·18	233·37	647·2
·2098	10	1·5285	7·795	66·880	21·76	213·43	510·6
	20	1·5118	7·486	66·647	21·52	212·32	
	30	1·49517	7·197	66·412	21·28	211·02	539·4
	40	1·4783	6 934	66·209	21·05	210·03	
	50	1·4618	6·687	65·994	20·81	209·06	568·7
·3103	10	1·4873	10·950	74·530	31·99	178·02	410·4
	20	1·4720	10·465	74·421	31·66	177·67	
	30	1·4565	10·026	74·343	31·33	177·41	437·6
	40	1·4411	9·621	74·267	30·99	177·17	
	50	1·4255	9·235	74·182	30·66	176·90	464·8
·4039	10	1·4494	14·197	79·477	41·41	155·50	346·7
	20	1·4350	13·543	79·506	40·99	155·56	
	30	1·4205	12·928	79·528	40·58	155·62	371·5
	40	1·4060	12·359	79·546	40·17	155·66	
	50	1·3916	11·853	79·593	39·76	155·78	396·6
·5001	10	1·4099	17·755	83·268	50·94	138·54	298·6
	20	1·3962	16·919	83·420	50·44	138·85	
	30	1·3825	16·123	83·549	49·95	139·10	321·5
	40	1·3689	15·406	83·690	49·46	139·39	
	50	1·3553	14·742	83·831	48·97	139·60	344·3
·5917	10	1·3726	21·39	86·113	59·90	126·23	263·8
	20	1·3597	20·29	86·299	59·34	126·55	
	30	1·3468	19·28	86·483	58·77	126·80	284·2
	40	1·3341	18·37	86·666	58·22	127·10	
	50	1·3213	17·55	86·871	57·66	127·51	305·3

TABEE II. (*cont.*)

Nitrobenzene and Carbon Tetrachloride.

C_2.	$t°$ C.	ρ_0.	ϵ_0.	P.	$n/N\times10^4$.	P_2.	$B\times10^{-2}$.
·7166	10	1·3224	26·48	89·128	71·93	113·31	227·3
	20	1·3106	25·06	89·375	71·29	113·66	
	30	1·2989	23·78	89·622	70·65	114·00	245·5
	40	1·2872	22·66	89·895	70·02	114·38	
	50	1·2754	21·70	90·218	69·37	114·84	264·4
·8046	10	1·2882	30·40	90·882	80·33	106·16	207·1
	20	1·2770	28·78	91·186	79·64	106·54	
	30	1·2658	27·33	91·502	78·94	106·93	224·0
	40	1·2546	26·00	91·819	78·24	197·32	
	50	1·2434	24·88	92·183	77·54	107·78	241·5
·8936	10	1·2539	34·71	92·480	88·73	100·16	190·1
	20	1·2433	32·79	92·810	87·98	100·53	
	30	1·2327	31·16	93·174	87·23	100·94	205·9
	40	1·2221	29·69	93·548	86·48	101·36	
	50	1·2115	28·47	93·972	85·73	101·83	222·3
1	10	1·2135	39·98	94·116	98·66	94·12	173·0
	20	1·2035	37·56	94·451	97·85	94·45	
	30	1·1935	35·46	94·805	97·03	94·80	187·3
	40	1·1836	33·67	95·180	96·22	95·18	
	50	1·1736	32·03	95·566	95·41	95·57	202·1

Debye theory. On the assumption that (n_1+n_2) A_1' can be calculated by extrapolation of the optical value, we get

$$P_3 = n_2 \frac{B'}{T}.$$

The number n_2 of the dissociated molecules, however, is now a function of the concentration as well as the temperature, and we can take P_3T to be proportional to the number of dissociated molecules at any dilution and temperature and a variation of P_3T as an indication of the variation of association.

There is, however, one difficulty in calculating P_3 which is generally overlooked. The value of A is generally taken to be, in all concentrations usually made, equal to the value at optical frequency, though specially in the case of polar molecules it is open to grave objections. The polar liquids are generally known to possess characteristic absorption-frequencies in the long wave-length regions, generally for wave-lengths of the order of a few metres, and an extrapolation over these critical frequencies seems scarcely theoretically justifiable.

We have, therefore, tried a different tentative calculation, and as the result seems encouraging, we venture to put forward the considerations, which are as follows :—

If, tentatively, we assume that the number of dissociated molecules at any dilution is given by a formula

$$n = N_0 e^{-\epsilon/KT},$$

where ϵ is of the nature of an energy threshold which determines association, and if, further, we assume that approximately the threshold value ϵ is determined by the residual electrical attraction between the dipoles, we can take

$$\epsilon \propto \frac{1}{Dr^2},$$

where D is the dielectric constant of the solvent, and r the average distance between the dipoles. Now, the average distance r can be taken to vary as $\frac{1}{n^{1/3}}$;

$$\therefore \quad \epsilon = \frac{\alpha' n^{2/3}}{D}.$$

The polarization P_2 will approximately be of the form

$$P_2 = A + \frac{BN}{T} e^{-\frac{\alpha' n^{2/3}}{DKT}},$$

or

$$\log (P_2 - A) = \log \left(\frac{BN}{T}\right) - \frac{\alpha' n^{2/3}}{DKT}.$$

It is found from Tables III. and IV. (pp. 276–278), as also from the Curve III., that remarkably enough, if the concentration be greater than ·1, the dielectric constant of the mixture of nitrobenzene and benzene or nitrobenzene and carbon tetrachloride can be represented accurately by the formula

$$\log (P_2 - 62) = \log \beta - \alpha n^{2/3}.$$

We have also found that the value of the ratio of α in the two cases varies almost inversely as the dielectric constants of the solvents. The values for lower concentrations, however, seem definitely to disagree with the above formula.

A comparison with the electrolytic dissociation theory will seem here not wholly out of place. It is well known that for binary electrolytes Ghose's formula, which is based on considerations very similar to the above, agrees very well with experiments; at high dilutions, however, there are slight discrepancies which can, on the other hand, be completely accounted for by the Debye-Hückel theory.

TABLE III.

Nitrobenzene with Benzene as solvent.

$(n/N)^{2/3}\times10^2$.	$\log_e(P_2-62)$.	$\log_e(P_2-62)+a(n/N)^{2/3}$.
·7798	5·4165	5·815
1·374	5·1108	5·812
2·172	4·6990	5·809
2·653	4·4545	5·810
3·047	4·2556	5·812
3·411	4·0725	5·815
3·846	3·8544	5·818
4·132	3·7087	5·819
4·555	3·4883	5·814

$a = 51{\cdot}07\ N^{2/3}$.

TABLE IV.

Nitrobenzene with Carbon Tetrachloride as solvent.

(1) 10° C.

$(n/N)^{2/3}\times10^3$.	$\log_e(P_2-62)$.	$\log_e(P_2-62)+a(n/N)^{2/3}$.
2·201	5·6935	
3·645	5·6480	
4·817	5·6065	5·861
6·218	5·5499	5·878
8·168	5·4630	5·895
10·0	5·3750	5·904
13·62	5·1882	5·909
16·79	5·0201	5·909
21·71	4·7538	5·903
25·78	4·5380	5·903
29·60	4·3378	5·905
32·98	4·1625	5·908
37·26	3·9380	5·910
40·11	3·7880	5·910
43·86	3·6418	5·911
46·0	3·4695	5·904

$a = 52{\cdot}81\ .\ N^{2/3}$.

TABLE IV. (*cont.*).

Nitrobenzene with Carbon Tetrachloride as solvent.

(2) 20° C.

$(n/N)^{2/3}\times10^3$.	$\log_e(P_2-62)$.	$\log_e(P_2-62)+a(n/N)^{2/3}$.
2·184	5·6602	
3·617	5·6215	
4·780	5·5824	5·833
6·170	5·5263	5·849
8·105	5·4433	5·870
9·926	5·3563	5·876
13·514	5·1756	5·883
16·67	5·0126	5·885
21·56	4·7508	5·880
25·61	4·5386	5·880
29·41	4·3419	5·882
32·77	4·1675	5·883
37·04	3·9447	5·884
39·88	3·7969	5·885
42·62	3·6516	5·883
45·74	3·4798	5·876

$a = 52{\cdot}38 . N^{2/3}$.

(3) 30° C.

2·166	5·6337	
3·588	5·5970	
4·741	5·5590	5·805
6·120	5·5042	5·822
8·041	5·4237	5·841
9·850	5·3386	5·850
13·41	5·1644	5·860
16·547	5·003	5·861
21·41	4·7485	5·858
25·44	4·5390	5·858
29·22	4·3451	5·861
32·567	4·1722	5·861
36·82	3·9513	5·860
39·64	3·8052	5·861
42·37	3·6620	5·860
45·49	3·4904	5·850

$a = 51{\cdot}87 . N^{2/3}$.

TABLE IV. (*cont.*)

Nitrobenzene with Carbon Tetrachloride as solvent.

(4) 40° C.

$(n/N)^{2/3}\times10^3$.	$\log_e(P_2-62)$.	$\log_e(P_2-62)+a(n/N)^{2/3}$.
2·148	5·6046	
3·559	5·5726	
4·703	5·5358	5·777
6·071	5·4848	5·796
7·977	5·4049	5·814
9·771	5·3220	5·824
13·31	5·1536	5·836
16·42	4·997	5·838
21·260	4·7460	5·836
25·27	4·5396	5·835
29·03	4·3489	5·837
32·36	4·1759	5·836
36·60	3·9585	5·835
39·41	3·8137	5·834
42·13	3·6726	5·833
45·24	3·5019	5·823

$a = 51{\cdot}31\,.\,N^{2/3}$.

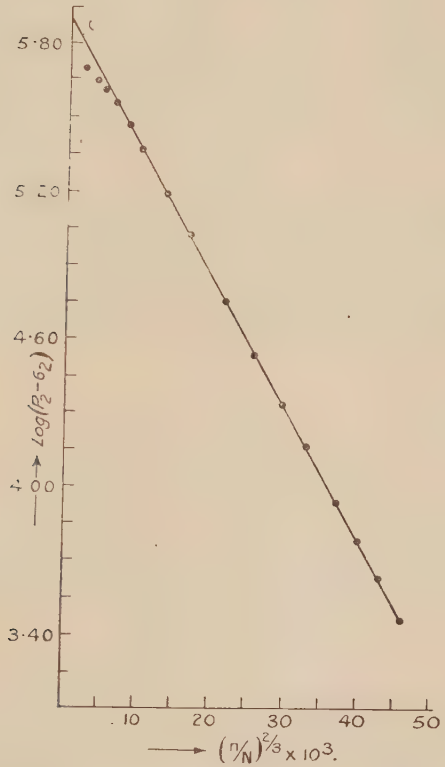
(5) 50° C.

2·131	5·5775	
3·529	5·5472	4
4·664	5·5114	5·749
6·022	5·4630	5·769
7·911	5·3882	5·791
9·694	5·3086	5·802
13·21	5·1437	5·815
16·300	4·9909	5·818
21·10	4·7440	5·818
25·10	4·5410	5·817
28·83	4·3516	5·818
32·15	4·1823	5·817
36·37	3·9673	5·816
39·17	3·8239	5·816
41·89	3·6842	5·814
44·99	3·5137	5·803

$a = 50{\cdot}87\,.\,N^{2/3}$.

Perhaps a more rigorous calculation on the same lines will explain the discrepancies at lower dilutions (the deviations are in the same sense in the two cases), as well as have the above simple formula as a limiting case for strong concentrations.

CURVE III.



For nitrobenzene with carbon tetrachloride as solvent at 10° C.

It is admitted, however, that it is rather premature to lay too much stress on this single case of nitrobenzene, and the author intends to collect more data about the different polar liquids to test the empirical formula.

The work already done, however, seems to point definitely towards the electrical origin of association in polar liquids.

TABLE V.

Moment of Nitrobenzene molecule.

Solvent.	t°C.	P_0c.c.	$(P_0-A)T \times 10^{-2}$.	Calc. $\mu \times 10^{18}$.	Solvent.	Author.	$\mu \times 10^{28}$.
Carbon tetrachloride	10	373	956	3·92	Benzene / CS_2	Lange	3·86
	20	359·3	956	3·92			
	30	350·3	961	3·94	CS_2 / Hexane	Williams*& Ogg	3·89
	40	343	970	3·95			
	50	335·3	976	3·96	Benzene	Williams†& Schwingel	3·90
Benzene	27	351	954	3·916	CCl_4 / Benzene	Author	3·94 / 3·92

A = 33.

* Williams and Ogg, Am. Ch. Soc. Jour. January 1928.
† Williams and Schwingel, Am. Ch. Soc. Jour. l. February 1928.

The author takes this opportunity of expressing his deepest gratitude to Professor S. N. Bose for his inspiring guidance and kind interest in the work.

University of Dacca,
Ramna, Dacca,
Bengal.

XXII. *On the Mechanism of the Electrodeless Discharge.* *By* JOHN THOMSON, *M.A., B.Sc., Ph.D., Lecturer in Physics in the University of Reading* *.

Introductory.

THE purpose of the present communication is to give a brief account of a simple theory of the discharge with external electrodes. It is not suggested that the treatment is either conclusive or exhaustive, but the expressions which emerge from the analysis are sufficient to explain many phenomena characteristic of this type of discharge. They also suggest possible lines of experimental attack. An application of the Tesla Coil transformer to the production of high-tension high-frequency oscillations is also discussed. The writer has been able, by this means, to obtain "electrodeless" discharges at relatively high gas pressures.

* Communicated by the Author.

The mechanism of the self-sustained discharge between metallic electrodes maintained at constant potentials is not yet clearly understood. The presence of the electrodes associated with the constant difference of potential between them causes the "life" of a gas ion to be very short indeed. This difficulty may in part be removed by the use of high-frequency alternating potentials; it may be almost entirely removed by applying the high-frequency oscillations to the discharge-tube by means of external electrodes. Under these circumstances ions produced in the discharge can only disappear owing to recombination or to diffusion to the walls, and consequently a self-sustained discharge will take place when the rate of formation of the ions is just more than sufficient to compensate for these losses. As a result it is unnecessary to postulate any ionizing mechanism beyond that due to collisions between electrons and molecules. The bulk of the electrons produced in this way remain in the field; they are not neutralized at an electrode after a relatively short "life." Hence the controversy which still exists concerning the action of the positive ions need not concern us.

Conditions for the Ionization of a Gas by a High-frequency Field.

Making the simplest possible assumptions, suppose a free electron to move under the action of an alternating electric field $E \cos \omega t$; then

$$m\frac{d^2x}{dt^2} = Ee\cos\omega t\ ;$$

whence, if $x=0=\frac{dx}{dt}$, when $t=0$,

$$\frac{dx}{dt} = \frac{E}{\omega}\frac{e}{m}\sin\omega t,$$

and

$$x = \frac{E}{\omega^2}\frac{e}{m}(1-\cos\omega t).$$

The assumption that $\frac{dx}{dt}=0$ at $t=0$ is, of course, an approximation; but since the velocity of agitation of an electron is of the order 10^5 cm./sec. at room temperature, and since the velocity producing ionization is of the order 10^8 cm./sec., the former may easily be neglected in comparison with the

latter. Relativity corrections have also been neglected for similar reasons.

The electron will have acquired sufficient energy to ionize a gas molecule colliding with it at time t, if

$$\tfrac{1}{2}m\left(\frac{\mathrm{E}}{\omega}\frac{e}{m}\sin\omega t\right)^2 > \mathrm{V}e. \quad . \quad . \quad . \quad . \quad (1)$$

where V is a gas constant related to the ionizing potential of the molecule. This is our first condition for ionization. The second condition must limit in some way or another the distance travelled by the electron while acquiring an ionizing velocity. For, should the electron collide inelastically with a molecule before attaining this velocity, or, conversely, should it not collide with a molecule until it had lost this velocity, then ionization would not in general occur. Writing this condition in the most general way to include the possibilities of a discharge at very low gas pressures,

$$\frac{\mathrm{E}e}{\omega^2 m}\left[2n+1+(-1)^{n+1}\cos k\pi\right] < \mathrm{L} \quad \text{if } k<\tfrac{1}{2}, \quad . \quad (2)$$

$$\frac{\mathrm{E}e}{\omega^2 m}\left[2n+1+(-1)^{n+1}\cos k\pi\right] > \mathrm{L} \quad \text{if } k>\tfrac{1}{2}, \quad . \quad (3)$$

where $\omega t=(n+k)\pi$, n is an integer, k is fractional, and L is a quantity proportional to the mean free path of the electron. These conditions state that when the electron is about to collide inelastically with a molecule it shall be moving with the ionizing velocity. Condition (2) applies to the case where the speed of the electron is increasing, condition (3) to the case where the speed is decreasing. The limiting values of k are supposed to be determined from condition (1).

At low pressures yet another condition becomes operative. If L for the electron is greater than the length of the discharge-tube, then, in order that the electrons should not be absorbed by the glass, the amplitude of the oscillations performed must be less than a certain length related in some way to the length of the tube, *i. e.*,

$$\frac{\mathrm{E}}{\omega^2}\frac{e}{m} < l. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

These four conditions are in themselves sufficient to define the electric field E and pulsatance ω, suitable for the production of ions at any pressure. However, as the pressure is varied, the four conditions vary in relative importance. For example, if the gas considered is air in

a tube 20 cm. long, and the pressure is greater than a certain minimum which is certainly less than 0·1 mm. of mercury, the fourth condition is of no importance, L being certainly less than l. Again, for frequencies less than 10^7 per sec., and so long as L is less than about 40 cm., ωt must be less than $\pi/2$, as defined by (1). Therefore, under these circumstances, conditions (2) and (3) may be written

$$\frac{\mathrm{E}}{\omega^2}\frac{e}{m}(1-\cos\omega t)<\mathrm{L}. \quad . \quad . \quad . \quad . \quad . \quad (2')$$

But to say that L is less than 40 cm. is to say that the pressure is greater than a minimum as yet undefined, but certainly less than 0·1 mm. in air. Hence, unless the pressure is very low or the frequency of the impressed voltage very high, our conditions simplify to the eminently workable form

$$\frac{1}{2}\frac{\mathrm{E}^2}{\omega^2}\frac{e}{m}\sin^2\omega t>\mathrm{V} \quad . \quad . \quad . \quad . \quad . \quad (1')$$

and

$$\frac{\mathrm{E}e}{\omega^2 m}(1-\cos\omega t)<\mathrm{L}. \quad . \quad . \quad . \quad . \quad . \quad (2')$$

If ωt is eliminated between these two conditions, remembering that $\omega t<\pi/2$, the resulting condition is

$$\mathrm{E}>\frac{\mathrm{V}}{\mathrm{L}}+\frac{\mathrm{L}\omega^2}{2e/m}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Write $\omega=2\pi\nu$, where ν is the frequency of the oscillation, and $\mathrm{L}=\mathrm{K}/p$, where p is the gas pressure ; then

$$\mathrm{E}>\frac{\mathrm{V}p}{\mathrm{K}}+\frac{4\pi^2\nu^2\mathrm{K}}{2pe/m}. \quad . \quad . \quad . \quad . \quad . \quad (5')$$

Now consider p/K as a variable x, and assume approximate values for the other constants. Let $\nu=10^7$, $\mathrm{V}=2\,.\,10^9$, and, since the velocities of the electrons are small compared with the velocity of light, let $\frac{e}{m}=\frac{e}{m_0}=1{\cdot}8\,.\,10^7$; then

$$\mathrm{E}>\mathrm{V}x+\frac{2\pi^2\nu^2}{ex/m},$$

or

$$\mathrm{E}>2\,.\,10^8\left(10x+\frac{1}{2x}\right).$$

Write

$$\mathrm{E}=2\,.\,10^8\left(10x+\frac{1}{2x}\right); \quad . \quad . \quad . \quad . \quad (6)$$

then equation (6) should represent with fair accuracy the mode of variation with the gas pressure of the electric field of frequency 10^7 per sec. necessary to produce ions by electronic collision. Going back to condition (5), and writing it as an equality, the mode of variation of the electric field with the frequency is obtained.

Conditions for the Maintenance of a Discharge.

If the ions did not recombine or diffuse to the walls, the four conditions already given would be sufficient to define the fields and frequencies necessary for a discharge. If, however, the rate of destruction of the ions due to diffusion is represented by βn, where n is the number of ions per c.c. at time t, and the rate of destruction due to recombination by γn^2, while the ions are being formed at rate αn, then

$$\frac{dn}{dt} = (\alpha - \beta)n - \gamma n^2,$$

whence

$$n = \frac{\alpha - \beta}{\gamma + (\alpha - \beta - \gamma)e^{-(\alpha-\beta)t}};$$

and when $t = \infty$,

$$n = \frac{\alpha - \beta}{\gamma}.$$

Hence, for a discharge to take place $\alpha - \beta$ must be very great relative to γ. The rate of recombination will not be a function of the gas pressure, nor will the rate of diffusion. Hence equation (6) will exhibit the mode of variation with the pressure of the field necessary to maintain the discharge; but the absolute value of E will not be given by the equation unless the losses due to diffusion and recombination are small. Townsend * states that there is no appreciable recombination in a high-frequency discharge, basing his conclusion on the experimental fact that the field necessary to produce a discharge is independent of the current. Recombination or some equivalent process must of course take place if the discharge is to be luminous.

Kirchner †, in an important paper on the subject of the high-frequency discharge, has given accurate curves showing the variation of the "maintainance potential" with the pressure. The discharge-tube which he used was furnished with internal electrodes, but under the conditions of his

* *Comptes Rendus*, clxxxvi. p. 55 (1928).
† *Ann. d. Physik*, lxxvii. p. 287 (1925).

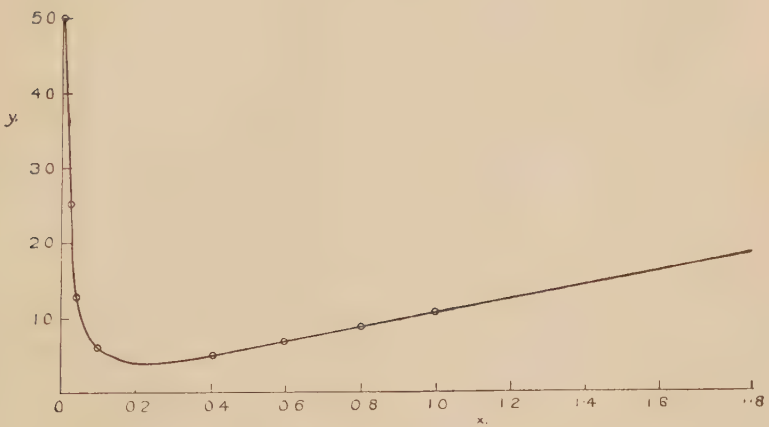
experiments these merely increased the rate of destruction of the ions. Otherwise (with certain restrictions as to electrode distances) the theory given above may be applied to his results A striking confirmation of equation (6) is obtained.

Fig. 1 shows the curve

$$y=10x+\frac{1}{2x}$$

Fig. 2 is a reproduction of two figs. from Kirchner's paper. Fig. 2 (*a*) exhibits the mode of variation of the potential necessary to maintain the discharge with the pressure in the gas oxygen, while fig. 2 (*b*) shows similar curves for air.

Fig. 1.



If the discharge is maintained by means of metallic rings surrounding the tube, the field due to the applied E.M.F. will not be uniform even when there is no electron current flowing. If there is a potential difference P between the rings at any instant, then the mode of variation of the electric field along the common axis of the rings is indicated in fig. 3, the distance between the rings measured along the axis being d, and the radius of the rings in this case being $d/3$. It will be observed that the maximum field in the region between the rings may be considerably greater than the mean field P/d. The components of the electric field are given by elliptic integrals, and a consideration of these has shown that the maximum variation in the resultant field takes place along the axis.

In the case of a discharge with external electrodes it is therefore not admissible to consider the electric field

Fig. 2 (*a*).

Oxygen.

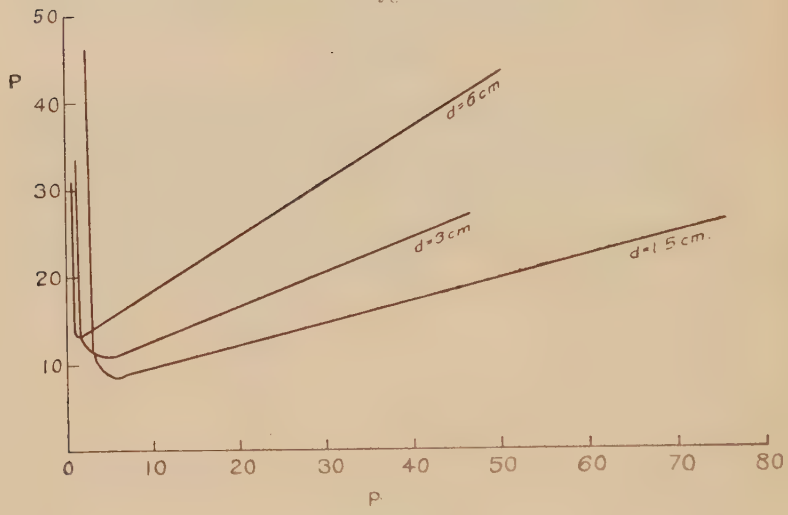
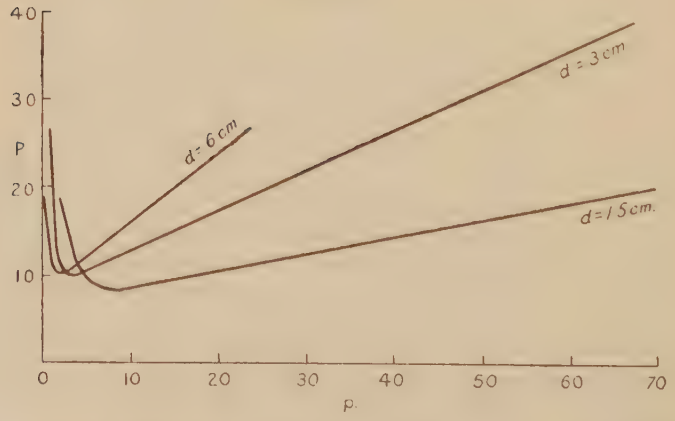


Fig. 2 (*b*).

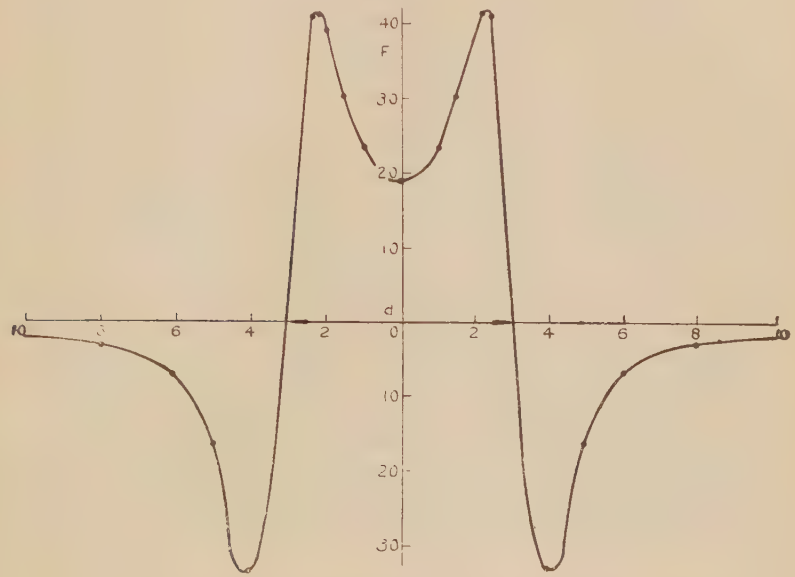
Air.



producing ionization as the mean field, but a first approximation to the field will be obtained by dividing the peak potential difference by the distance between the rings.

In the case of a discharge with internal electrodes the variation of the field along the axis is not so marked, and the mean field will give a better approximation to the ionizing field. It is to be expected that the passage of any considerable current through the gas will further disturb the electrostatic distribution of potential.

Fig. 3.



If, as a first approximation, we assume $E = P/d$, where P is the peak potential difference between the electrodes, and d their distance apart, then equation (6) becomes

$$P = 2 \cdot 10^8 d \left(10x + \frac{1}{2x}\right),$$

and when x is large the curve becomes a straight line whose gradient is proportional to d. This is also indicated unequivocally by Kirchner's curves. The fact that the potential difference between the electrodes producing a discharge is a linear function of the distance between the electrodes has also been noted by Townsend, Gutton, and others, and has led them to draw analogies between the high-frequency discharge and the positive column of a "straight" discharge.

Returning to the condition (5′), and writing the limiting equation

$$P = V\frac{pd}{K} + \frac{2\pi^2\nu^2 K d}{p\, e/m}, \quad \ldots \quad (7)$$

P has a minimum value given by

$$\left.\begin{aligned} P_m &= 2V\frac{pd}{K} \\ p_m^2 &= \frac{2\pi^2\nu^2 K^2}{V\, e/m} \end{aligned}\right\} \quad \text{when} \quad \ldots \quad (8)$$

Kirchner's values for the constants involved should be fairly accurate when the distance between the electrodes is reasonably large, and so we take his curve for $d=3$ cm., the gas being air, $\nu = 3{\cdot}5 \cdot 10^7$ per sec., $P_m = 4{\cdot}6 \cdot 10^9$ e.m.u., $p_m = 3 \cdot 10^{-3}$ cm. of mercury. Substituting in equations (8) we find $V=4$ volts, $K = 2 \cdot 10^{-3}$, whence $L=200$ cm. when $p = {\cdot}0001$ mm. At this pressure the mean free path of the electron in air as calculated from the kinetic theory of gases is about 400 cm. Hence equation (7) not only predicts the experimental curve, but gives at least the correct order for the constants involved. Possibly the agreement between experiment and theory would be closer if accurate data were available for the discharge with external electrodes. The agreement obtained appears to indicate that the rate of destruction of ions at this frequency is negligible.

Condition for a Discharge at any Pressure.

From condition (1) no discharge can take place at any pressure whatsoever unless

$$\frac{E^2}{\nu^2} > \frac{8\pi^2 V}{e/m} \quad \ldots \quad (9)$$

Now Kirchner finds that with $\nu = 3{\cdot}5 \cdot 10^7$ the minimum E is of the order $1{\cdot}5 \cdot 10^9$ e.m.u. Assuming $V = 2{\cdot}6 \cdot 10^8$ for the gas, which was neon,

$$\frac{E^2}{\nu^2} \doteqdot 2 \cdot 10^3,$$

while

$$\frac{8\pi^2 V}{e/m} \doteqdot 10^4.$$

Again the quantities are of the correct order of magnitude. If cumulative ionization takes place (and in neon this is very probable), V might easily be one-fifth of the assumed value. Kirchner's values for E are maintainance values. The fields required to start a discharge he finds unreliable, but about three times the maintainance values (in the case of air). Hence it may be supposed that for the discharge to start, the electron must first fall through a potential comparable with the ionization potential. When the discharge is once started, however, the probability of cumulative ionization occurring is great, and the value of V in our equations diminishes greatly. This is equivalent to saying that the ionization efficiency of the electrons varies with the electron density. Apart altogether from such conjectures, it may be seen that equation (9) correctly predicts the possibility of a discharge with potential differences smaller than the ionizing potential of the gas.

Variation of the Maintainance Potential with the Frequency.

The equation (7) suggests that as the frequency of the applied E.M.F. increases the potential necessary to produce a discharge also increases. It must be observed, however, that at high gas pressures the term $\frac{2\pi^2\nu^2 \mathrm{K}d}{p\,e/m}$ is relatively unimportant, unless ν is very large indeed. As has already been shown, the variation of P is then given approximately by

$$\mathrm{P} = \mathrm{V}\frac{pd}{\mathrm{K}}.$$

Also, the losses due to diffusion of the electrons will depend in some way on the frequency of the E.M.F. It might be suggested that the greater the amplitude of their free oscillations the greater the losses would be. This would obviously be the case with internal electrodes. But the amplitude varies inversely as the square of the frequency, and consequently it might be expected that the greater the frequency the smaller the diffusion losses would be. It is therefore suggested that the complete expression for the discharge potential ought to contain a factor $\phi(\nu)$ such that it decreases as ν increases—*i. e.*,

$$\mathrm{P} = \phi(\nu)\left[\mathrm{V}\frac{pd}{\mathrm{K}} + \frac{2\pi^2\nu^2 \mathrm{K}d}{p\,e/m}\right]. \quad . \quad . \quad . \quad (7')$$

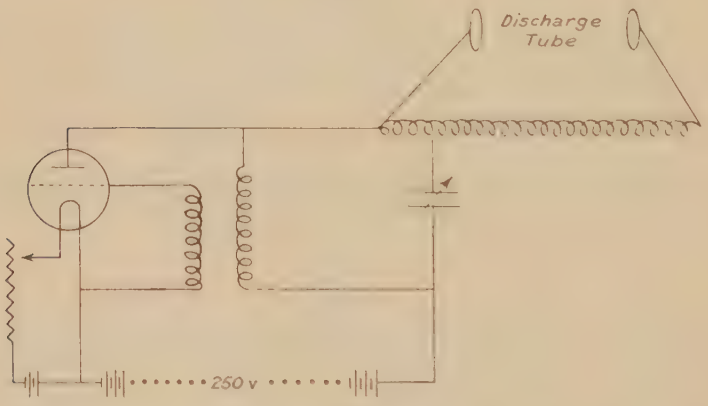
This is also suggested by the condition (4).

Summarizing the results of the preceding discussion, it may be said that the high-frequency discharge may obviously be maintained by the ionization produced only by electronic collisions. The equations and conditions derived from this hypothesis are sufficient to explain the mode of variation of the maintenance potential with the pressure. The magnitudes of the gas constants obtained from them are at least of the correct order. Also, while the mode of variation of the maintainance potential with the frequency is not given by the simple equation derived, other considerations at least indicate how the experimental facts might be explained.

The Application of the Tesla Transformer to the Production of High-Frequency Discharges.

The circuit employed by the writer is shown in fig. 4. Large alternating currents of approximate frequency 10^6

Fig. 4.



were produced by means of four Marconi T 15 valves in parallel. This current was sent through the bottom four or five turns of a Tesla Coil. The latter contained about 130 turns of stout copper wire of radius 15 cm., the turns being about 1 cm. apart. Peak voltages of about 4000 were obtained across the whole coil. By means of a variable condenser in the oscillating circuit the applied frequency could be varied. Exceedingly sharp resonance was obtained with the Tesla Coil, and consequently a small variation in the capacity controlled the potential applied to the discharge-tube without seriously altering the frequency. In this way

discharges were obtained at pressures ranging from 0·01 mm. to 10 mm. The remarkable striations examined by Richards * were observed. This appears to be a very suitable method for the production of high potentials at a frequency of a million per second.

Physics Department,
The University of Reading,
March 24th, 1930.

XXIII. *A Modification of Michelson's Beam Interferometer.* *By* E. H. Synge †.

THE present limitations to Michelson's Beam Interferometer are of a mechanical nature. The length of a rigid metal beam, which is light enough to be carried on the structure of a moving telescope, cannot be increased indefinitely; and the resolving power of the apparatus is thus limited by purely mechanical difficulties.

It seems possible to escape altogether from these limitations by substituting two small cœlostats, arranged in a certain way, for the massive moving telescope frame and metal beam of Michelson's arrangement. A modification of the apparatus on these lines will be discussed in the present paper.

The essential feature of the arrangement suggested is the relative position of the two cœlostats. When these are placed *so that their axes (which, of course, are polar axes) form part of the same geometrical right line*, it is evident that their reflecting surfaces can be set so as to form part of the same plane, and, when so set, the two cœlostats virtually form part of one large cœlostat. If a long base-line is desired the cœlostats must clearly be placed on a hill-side with a north-south slope equal to the latitude. At the Equator this becomes a north-south alignment on the same level.

Once it is seen that we can in this way form what, for the purpose of stellar interferometry, is virtually one large cœlostat of almost unlimited size, it becomes obvious that the two cœlostats can be used, in conjunction with a fixed

* Phil. Mag. ii. p. 508 (1926).
† Communicated by the Author.

telescope, to obtain a resolving power which is proportional to the distance between the cœlostats multiplied by the cosine of the declination of the star under consideration. Accessory plane mirrors must, of course, be employed, these being adjusted so that the two beams from the star, which are reflected by the two cœlostats, ultimately pass down the sides of the fixed telescope, and arrive together in the centre of its focal plane, with equality of optical path-lengths, as measured from any arbitrary wave-front in space. Thinking of the two cœlostats as parts of one large cœlostat, we see at once that if there is this equality at any moment there will be equality at every moment. If the cœlostats are not quite in correct alignment a continually increasing retardation of one beam upon the other will indicate what further adjustments must be made.

For stars of a different declination there must obviously be a rearrangement of the accessory plane mirrors, and the apparatus should be designed so that such rearrangement can be carried out readily. Where the base-line is long the simplest plan would perhaps be the following:—The telescope can be moved along a rail which is parallel to the axes of the cœlostats, *i. e.*, is a polar axis. As it moves it preserves its direction. The telescope is fitted with two mirrors, corresponding to the inner mirrors of Michelson's arrangement, the line joining the centres of these mirrors being parallel to the common axis of the cœlostats. Each cœlostat has two plane mirrors near it, which can be adjusted to throw a beam from the cœlostat in any direction. For any given declination these mirrors are arranged so that each of the two beams strikes the corresponding mirror attached to the telescope at the proper angle to bring it ultimately to the focal centre. Care is taken that the two beams have no rotation with respect to one another as they pass into the telescope. That is, each cœlostat shows the same field, in the same orientation, if used independently with the telescope. An approximate equalization of path-lengths is obtained by moving the telescope along the rail, final equalization being effected by similar methods to those used by Michelson.

In comparing such an arrangement of cœlostats with the present form of Beam Interferometer the following points may be noted :—

(1) The optical principles are exactly the same. The resolving power is not, however, proportional to the

distance between the cœlostats, but to this distance multiplied by the cosine of the declination of the star.

(2) The stellar diameters which can be measured are north-south diameters, and no others. This, as a rule, will be of very little consequence.

(3) The stars very near the celestial poles cannot be dealt with.

(4) The practical limits to the resolving power, apart from atmospheric or other disturbances, depend on latitude and local topography. At the Equator these limits recede almost indefinitely.

Since the ultimate possibilities of the arrangement seem to depend almost entirely on the effect of atmospheric or mechanical disturbances, it may be of interest to consider these in some way which will help us to estimate how far they are likely to impose practical limits on the distance between the two cœlostats. To understand the effect of such disturbances upon the fringes it is necessary, in the first place, to be quite clear about the optical principles which are involved in Michelson's use of plane mirrors to increase the resolving power. This matter is, perhaps, not treated with sufficient fulness in the text-books. Everything is no doubt contained in the general principle which is invoked in Schuster and Nicholson's 'Optics' (3rd edition, pp. 167 F, G). But not every reader is likely to see immediately how this principle leads to the observed phenomena. Indeed, to what else but some difficulty or obscurity in the connexion, can one ascribe the singular fact that Michelson's brilliant idea lay neglected for thirty years after he had published it in 1890, obtaining no recognition whatever until he had himself carried it into effect experimentally ?

Anyone who is not perfectly clear as to the formation of the fringes will probably find it worth while to work out the matter at length. The slits need not be taken, where they would be situated in practice, after the various reflexions. It is immaterial to the result where they are placed, and the writer, at all events, finds it more easy to follow the rays when the slits are placed immediately above the pair of distant mirrors in Michelson's arrangement.

Turning to the disturbing factors : mechanical disturbances will probably be quite negligible if two cœlostats are used. Any slight effects of this kind should be lost in the atmospheric disturbances, which are our real

concern. As regards these: if we take Michelson's symmetrical arrangement, with the telescope directly pointed at a star, and suppose that slits, S_1 and S_2, are opened above the distant pair of mirrors, and that these slits are narrow, and if we assume that no disturbances between the slits and the focus of the telescope need be reckoned with, it appears that the alterations in the fringes may be occasioned in two ways, which can be dealt with separately. (1) The wave-front at one slit, S_2, may have a retardation or advance on the wave-front at he other slit, S_1. (2) The wave-front at S_2 may be inlined at some angle θ_2 to the norm-plane which would represent the wave-front in ideally calm conditions of the atmosphere, while the wave-front at S_1 may be inclined at an angle θ_1 to the same plane, and θ_1 and θ_2 will not, in general, be equal to one another.

Of these two irregularities, (2) does not produce any displacement of the fringes, but only changes their intensity. Provided that there is no retardation of a wave-front at one slit on the corresponding wave-front at the other slit, the central fringe, for white light, will remain fixed in the centre of the focal plane, no matter what θ_1 and θ_2 may be, so long as the fringes are visible at all. This seems remarkable at first sight, and yet it is really self-evident; for, no matter what θ_1 and θ_2 may be, those diffracted rays from S_1 and S_2 which reach the central point of the focal plane are of exactly equal optical length, as measured from S_1 and S_2 to that point. Under the supposed circumstances, these rays will therefore form the centre of the central white fringe at the point in question. Possibly the remark made by several writers, that the steadiness of the fringes is inadequately explained by the theory, is due to an insufficient recognition of this point.

The displacement of the fringes is entirely due to the factor (1). There will be a displacement from bright to dark for every half wave-length of retardation which the wave-front at one slit has with respect to that at the other.

We may now consider how far the motion of the fringes is likely to depend on the length of the base-line; and it will be well to form some kind of working conception of the atmospheric disturbances. Taking, as before, the symmetrical arrangement of Michelson, with a moving telescope, and neglecting certain variations which would occur

in a calm atmosphere, we will consider a point p above one of the distant mirrors, and fixed relatively to the telescope, which, of course, supplies our frame of reference. A plane P, drawn through p, will represent the wave-front of a star for ideally calm conditions of the atmosphere, and if the telescope is pointed directly towards the star this plane will cut the axis of the telescope at right angles. If the atmosphere is not perfectly calm the wave-fronts for various instants will be represented by a group of undulating surfaces drawn through p. In the simplest case the plane P will be the mean, or norm, of this group, and no matter how far the two mirrors may be distant from one another, we may assume that, for this case, the wave-fronts will not depart from the norm by more than a certain amount which attains a maximum at quite a small distance from p. The case resembles somewhat that of the undulating surface of the sea, and would probably answer to the actual phenomena for the atmosphere, if the disturbances had no sort of coherence—if they were not caused by any definite travelling bands of air.

To obtain a better approximation to the facts it will be necessary to consider the norm of the wave-fronts as being no longer a fixed plane P, but an undulating surface P′, moving with a larger, slower motion than that of the wave-fronts with respect to it. We might pass on to a further approximation, and consider the norm of P′ at various instants. But for our purposes it will probably be sufficient to think of the wave-fronts drawn through p as undulating rapidly about a surface P′, which itself has a large and comparatively slow motion. We have to deal with the superposition of these effects. As regards the motion of P′, this effect is likely to increase both in range and in rapidity as we proceed further from p. But the motion should have a certain steadiness. Its rate of change should not vary rapidly. The various methods used by Michelson to equalize the path-lengths might be adequate to counteract it. But a more powerful method would consist in carrying the beams through closed pipes containing air, the pressure of which could be altered at will by some means which would not produce currents of air in the pipes. For instance, a narrow rubber tube might be laid in the pipe, and the increase or decrease of pressure inside the tube would be conveyed to the air outside it in the pipe with little disturbance. Some device for continu-

ously altering the pressure at varying rates, the operator simply controlling the rate, would probably make it possible to deal with the most rapid motion P′ might have under ordinary circumstances. It should be added that, although the motion of P′ would tend to increase with increase of base-line, the former increase would certainly not be proportional to the latter. And after a certain, not very great, distance, the motion of P′ would probably reach its maximum. As regards the rapid small undulations about P′, it is clear, on the assumptions made, that these should produce no more rapid displacement of the fringes when the mirrors are very distant than when they are comparatively close.

From these considerations one seems justified in expecting that atmospheric disturbances, under favourable conditions, will not impose any limit on the length of base-line which may be used. Everything that has been said is, of course, applicable without essential change to the case of two cœlostats. If these were very far apart it would certainly be desirable to conduct the beams the whole way from the cœlostats to the telescope through partially evacuated pipes. Michelson mentions an experiment * in which he conducted beams in opposite directions round a circuit of a mile in partially evacuated pipes, and obtained fringes which were capable of accurate measurement to one hundredth part of a fringe. With the much less accuracy which is necessary, or possible, in the case of the stellar interferometer, it seems that beams might be satisfactorily conducted through pipes of many times this length; and it is not inconceivable that, at the Equator, results might be obtained with two cœlostats over a base-line a thousand times as great as would be practicable with the Beam form of apparatus.

From the foregoing discussion it might appear that the reflecting surfaces of the two cœlostats must necessarily be adjusted to form part of one plane. But this is not an essential condition. It depends on the arrangement of the accessory mirrors. Indeed, siderostats could probably be substituted for the cœlostats with advantage. The most convenient plan might even be to replace the cœlostats by two small reflecting telescopes, mounted equatorially. In each of these a small convex parabolic

* A. A. Michelson, 'Studies in Optics,' p. 164.

mirror would be substituted for the Cassegrain hyperbolic reflector. Narrow parallel beams would thus be obtained which would be reflected along the polar axes, supposing this part of the instruments to be made hollow, as has been done in some telescopes. With this arrangement the principal telescope might be greatly reduced in size, as can easily be seen, the general principle invoked by Schuster and Nicholson still holding good for the optical theory. The collinearity of the polar axes, considered as geometrical lines, of the two other instruments, is of course an essential condition in all cases, whether cœlostats, or siderostats, or subsidiary telescopes are in question.

XXIV. *Absorption in Hydrogen Gas of Hydrogen Positive Rays.* *By* A. C. Law, *M.A.*, *and* G. Mutch, *M.A.**

Introduction.

ACCORDING to the theory of the absorption of electrified particles positive rays are absorbed by electron collisions, and have, like α-rays, a definite range. On the other hand early experiments with non-homogeneous positive rays showed there was considerable absorption for rays of all energies; the absorption was exponential and did not vary much with the energy of the rays. Wien †, Königsberger and Kutschewski ‡, Ruchardt §, and Conrad ¶ have studied this problem, and found values for the absorption coefficient in various cases. It should be noted that these experiments, with the exception of one by Ruchardt and that by Conrad, were made with non-homogeneous rays.

Wien found, by using a thermo-element, that the absorption coefficient of positive rays in hydrogen gas was not proportional to the pressure. Conrad showed that most of the diminution in intensity of positive rays passing through hydrogen at the order of pressures and velocities

* Communicated by Prof. G. P. Thomson.

† W. Wien, *Ann. der Phys.* xxiii. p. 485 (1907); xlviii. p. 1089 (1915); lxx. p. 1 (1923).

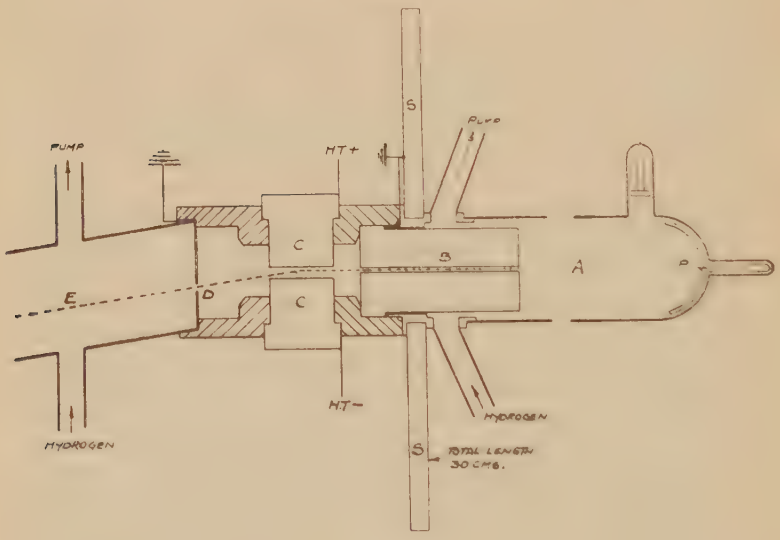
‡ Königsberger and Kutschewski, *Ann. der Phys.* xxxvii. p. 161 (1912).

§ E. Ruchardt, *Ann. der Phys.* lxxi. p. 377 (1923).

¶ R. Conrad, *Zeit. für Phys.* xxxv. p. 73 (1925); xxxviii. p. 465 (1926).

here considered, as measured by his apparatus, was caused by spreading. Further, Conrad determined experimentally that the spreading exponent for hydrogen positive rays in hydrogen was directly proportional to the pressure. In a preliminary experiment by one of the authors, using non-homogeneous rays and employing a method as described below for homogeneous rays, the absorption was found to be exponential, but no definite relation could be obtained between absorption coefficient and pressure of the hydrogen gas or the velocity of the rays. To simplify the problem it was decided to use homogeneous positive rays.

Fig. 1.



Apparatus.

Fig. 1 is a sketch of the apparatus.

The positive rays are produced in the discharge-tube A, and pass through a hole 2 mm. in diameter, 7·75 cm. long, in the cathode B, which is made of Swedish iron. The length of the cathode is such that the positive rays have reached a steady state before entering the deflecting chamber. A magnetic shield S of stalloy stampings is built up round the cathode to prevent the magnetic field deflecting the positive rays into the cathode itself. The rays then pass between two magnetic pole-pieces C (3 cm. ×

1·5 cm.), which can be utilized also for an electric field by suitably connecting to a battery, since the pole-pieces are mounted in an ebonite cylinder. Knowing the dimensions of the apparatus and the strengths of the magnetic and electric fields, a portion of the positive ray parabola of known energy can be made to pass through the slit D in an aluminium earthed disk. The slit is so placed that the mean deflexions are: magnetic 1·636 cm., electric 0·825 cm. The distance from the end of the fields to the aluminium disk is 3·5 cm. A small glass slide, coated with willemite, is fixed in the aluminium disk in the quadrant adjoining the slit, so that by reversing the magnetic field the positive ray parabolæ can be observed, and the one corresponding to the hydrogen atoms chosen by altering the field strengths. In the other two quadrants there are holes, so that the pressure is the same on both sides of the disk. The resulting beam of positive rays, which is fairly homogeneous, passes along an observation chamber E, where the absorption is measured. The far side of E is painted dull black inside, and baked before assembly. This prevents the reflexion of the light of the beam.

The discharge-tube and observation chamber are exhausted by a mercury diffusion-pump backed by a water-pump, mercury vapour being prevented from entering by a suitable trap. Hydrogen gas can be allowed to enter either chamber at will. A pyrex glass shield, P, at the anode end of the discharge-tube prevents the end of the tube being melted by the intense cathode ray bombardment.

Method.

A photographic method is used to get the intensities of the positive ray-beam at different points along its course, and from these the absorption is found. The experiments of Königsberger and Kutschewski showed that within fairly wide limits of pressure and velocity the velocity of the positively charged atoms is not appreciably altered by their passage through the gas. So it was assumed here that the intensity of the light emitted at any point in the beam was proportional to the number of positively charged atoms present at that point.

A photograph of the light originating in the beam is taken with a camera having a lens of numerical aperture 2

and a movable plate-holder, so that a series of photographs can be taken on the same plate by exposing successive strips of it. Fast plates (650 H. and D.), which are "backed" to prevent reflexion, are used in order to reduce the time of exposure to three hours.

A characteristic curve for the photographic plate is constructed, showing the relation between the intensity of the light incident on the plate and the density of the image. From the density of the image of the beam and the characteristic curve the intensity of the light emitted along the positive ray-beam can be calculated, and hence the absorption found.

The method of constructing the characteristic curve for the plate is as follows:—An optical wedge is placed in front of the brightest part of the beam, with its gradation at right angles to the axis of the positive ray-beam. A photograph of this part of the beam is then taken. A series of such exposures is taken on the same plate, the wedge being moved a known distance for each one. The time of exposure for these and also for the whole beam is three hours. The whole photographic plate, with the latent image of the beam and those for the characteristic curve, is developed, due precautions being taken to get uniform development. The density of the darkest part of each image on the plate for the characteristic curve is measured by a photometer, and a curve plotted between the density of the image and 10^{-kx}, where k is the wedge-constant and x is the distance the wedge has been moved from zero position for that image. Fig. 2 shows a curve so obtained. Now the intensity of the light passing through the wedge is given by $I = I_0 10^{-kx}$, so that actually fig. 2 gives the relation between the density of the photographic image and the intensity, in arbitrary units, of the light which made it.

The only variable factor affecting the amount of blackening of the plate is the intensity of the light falling on it. For accuracy in constructing the intensity-density curve it is essential that the intensity photographed should not alter except by movement of the optical wedge. It is impossible in practice to keep the discharge-tube under constant conditions for three hours, neither is it possible to obtain exactly the same conditions from day to day. In these experiments it is assumed that, providing the voltage applied to the discharge-tube and the current through

it remain constant, the intensity of the beam of positive rays is the same. This assumption is justified by the fact that the points obtained lie on a smooth curve of the expected shape, as in fig. 2. This is confirmed too by the

Fig. 2.

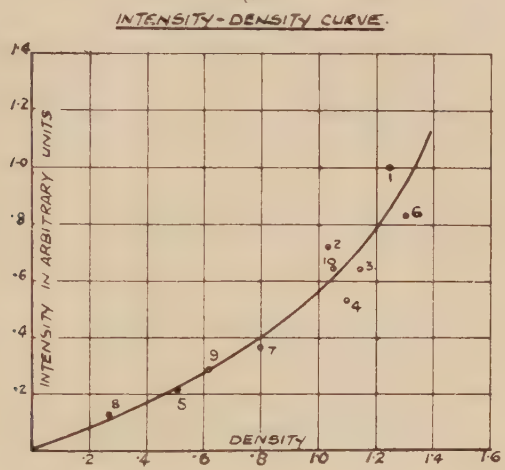


TABLE I.

Photograph.	Pressure mm. 1000 of Hg.	Current. milliamps.	Spark gap. cm.	Wedge. cm.	Density of image.
1	9 to 12	2	0·53	0	1·25
2	9 to 13	2	·53	0·3	1·028
3	10 to 18	2	·54	0·5	1·145
4	10 to 18	2	·53	0·7	1·11
5	12 to 19	2	·53	1·7	0·515
6	12 to 20	2	·48	0·2	1·30
7	12 to 21	1·9	·48	1·1	0·80
8	12 to 20	2	·54	2·3	0·27
9	13 to 19	2	·53	1·4	0·62
10	10 to 19	1·9	·54	0·5	1·05

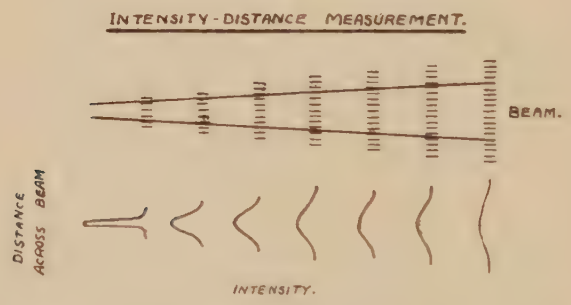
fact that similar results are obtained using the intensity-density curve when the densities of the photograph of the beam cover the whole range of the curve or only part of it.

The results from which fig. 2 is constructed are given in Table I. All these exposures were made on one plate.

By measuring the density at any point of the photographic image of the beam, and using the intensity-density curve, the intensity of the light emitted at the corresponding point of the beam is obtained. The density of the photographic image is measured at small intervals across it, *i. e.*, at right-angles to the direction of the beam, and these densities are converted to intensities as above. Intensity of the light is then plotted against distance across the beam. The resulting curve is, as it were, a cross-section in intensity of the beam at that distance along the beam. Fig. 3 shows the type of curve obtained at various distances.

The areas of these curves are proportional to the light incident on the plate at these distances along the beam.

Fig. 3.



They are not, however, proportional to the total light emitted from the corresponding sections in the beam of positive rays. Owing to the obliquity of the rays of light from the ends of the beam the corresponding densities are too small. If a ray of light makes an angle θ with the axis of the lens of the camera at its centre O, r is the distance of the point P in the beam considered from O, d is the perpendicular distance from O to the beam, and A the area of the lens, the solid angle subtended by the lens at P is $A \sin(90-\theta)\ r^2$ or $A \cos\theta\ r^2$. Hence the total amount of light from an element δx of the beam at P, which passes through the lens and goes to form an image, is $I_x \delta x A \cos\theta / r^2$, and the intensity of the image will be proportional to this, *i. e.*, to $I_x \delta x A \cos^3\theta / d^2$, since $\frac{d}{r} = \cos\theta$. Hence the measured intensity of the light at a point in the

beam will be less than the true intensity in the ratio $\cos^3\theta$ to 1.

The distance from the beam to the lens is 36 cm., and the magnification of the image is 0·149. The photographs obtained of the beam are about 4·5 cm. long and 0·25 cm. to 0·4 cm. wide.

Experimental Results.

Table II gives the results of the experiment.

TABLE II.

Atomic Rays (Protons).

Pressure mm./1000 Hg.	Intensity in arbitrary units.										
Distance along photo.	0·25	0·75	1·25	1·75	2·25	2·75	3·25 cm.				
9	258	214	222	244	233	130					
10	494	487	503	494	424	363	265				
20	732	636	646	565	535	482	324				
30	413	265	234	177	146	167					
Distance along photo.	0	0·3	0·6	0·9	1·2	1·5	1·8	2·1	2·4	2·7	cm.
15	723	744	798	726	766	736	677	657	597	539	

The energy of the positive rays was 10,800 volts.

Fig. 4 shows the results contained in Table II graphically.

Discussion.

It will be seen that the absorption of homogeneous positive rays by hydrogen is definitely not exponential. On the contrary, most of the beams show a sharp decrease of intensity, which seems to indicate the existence of a range for the particles. It is important to note, however, that the method of the experiment breaks down when the velocity of the particles changes appreciably, so that no definite conclusion can be drawn as to the length of the range, but the experimental results can be compared in a general way with the results given by theory.

When Thomson's formula* for the range of an electrified particle was applied to these results the range calculated

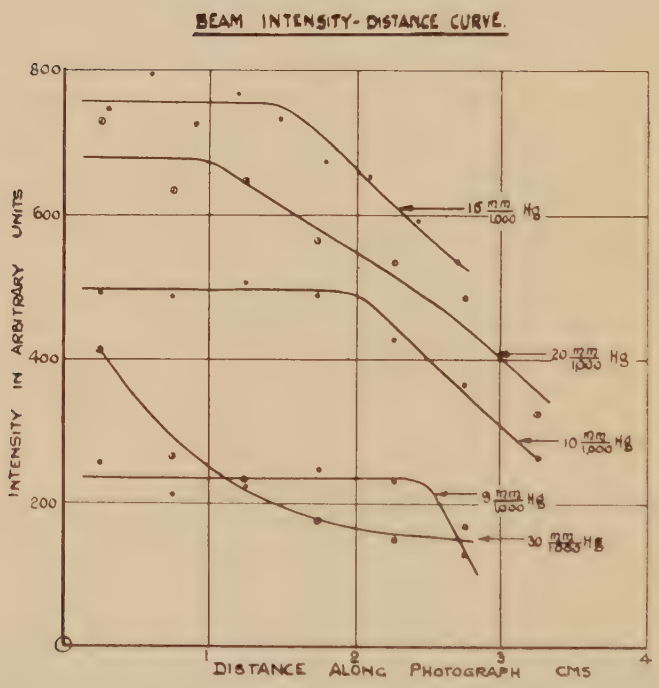
* 'Conduction through Gases,' p. 376.

was much greater than the range found by experiment. Bohr's formula* for hydrogen breaks down completely when applied to atoms of the velocity here considered.

Now Henderson's theory †, as modified by Fowler ‡, gives

$$\frac{d'T}{dx} = -\frac{2\pi e^4 N}{mV^2} \log_e \frac{4P}{\lambda},$$

Fig. 4.



where T is the Kinetic Energy ; e is charge on an electron ;

N is number of electrons per unit volume ; m is mass of an electron ;

V is velocity of the atomic rays ; P is the energy of the ray in E.S.U.

λ is the first resonance potential.

* Bohr, Phil. Mag. xxv. p. 10, and xxx. p. 581.
† Henderson, Phil. Mag. xliv. p. 680.
‡ Fowler, Camb. Phil. Soc. xxi. p. 521.

Taking $\lambda = 10$ volts, and protons of 10,800 volts energy gives

$$\text{Range} = \frac{880}{p}.$$

The authors find for rays of 10,800 volts energy a marked drop in the intensity of the beam at a distance d on the photographic plates as obtained from fig. 4 and tabulated below.

TABLE III.

p 1000 mm. Hg.	d on plates, cm.	$\frac{d}{0{\cdot}149}$ cm.	$x = \frac{d}{0{\cdot}149} + 5$ cm.	px.
9	2·4	16·1	21·1	190
10	2·0	13·4	18·4	184
20	1·0	6·7	11·7	234
30	< 0·5	< 3·3	< 8·3	< 249
15	1·5	10	15	225

x is the actual distance the beam has travelled from the middle of the electric and magnetic deflecting fields where the energy is measured to that point where a marked drop in the intensity of the beam occurs.

Taking a mean value of px as 216, this theory also gives too long a range. This being so, the method of experiment breaks down. But it is clearly the case that the absorption of positive rays is due to a gradual stopping.

These results are not inconsistent with the results obtained by Königsberger and Kutschewski. They found that with rays of velocity $2{\cdot}3 \times 10^8$ cm. per second the change of velocity in passing through 16 cm. of hydrogen at 3×10^{-3} mm. of mercury did not exceed 0·5 per cent. A calculation based on Henderson's formula gives the change of velocity as 0·46 per cent. under the same conditions.

General Conclusions.

1. The absorption is not exponential. Hence it is not a case of the removal of particles by sudden stoppage or large angle scattering.

2. It follows that the decrease in velocity must be gradual and an important factor.

3. This prevents the method from giving quantitative results.

4. The distance at which a rapid decrease in luminosity occurs is probably the place at which the energy is so reduced that the emitting power is seriously diminished.

5. The diminution in velocity predicted by Henderson's formula does not seem enough to account for the observed diminution in luminosity. This is not surprising in view of the failure of the formula for α-rays. A factor of 2, which is needed in the latter case, would make the results plausible.

The authors desire to express their thanks to Prof. G. P. Thomson for suggesting this problem, for many helpful suggestions, and for his continued interest in it, and their appreciation of the technical assistance given by Mr. C. G. Fraser and his staff in the Natural Philosophy Department of the University of Aberdeen.

XXV. *An X-ray Investigation of the Crystals of Azobenzene.* *By* Mata Prasad *.

THE crystal structure of azobenzene has been studied by Becker and Jancke †. They examined the substance in the state of a compressed powder by a method that combined that of Bragg and of Debye and Scherrer, and found the dimensions of the unit cell to be

$$a=12{\cdot}50\ \text{Å.},\quad b=5{\cdot}28\ \text{Å.},\quad c=8{\cdot}38\ \text{Å.},\quad \beta=116^\circ,$$

the axial ratio being

$$a:b:c=2{\cdot}370:1:1{\cdot}590.$$

They found the density of the crystals to be 1·235. These data indicate that the unit cell contains two molecules.

Bragg examined the crystals by the Ionization Spectrometer method, and concluded that the unit cell contains four molecules ‡.

Crystals of azobenzene, ($C_6H_5-N=N-C_6H_5$), were prepared by the slow evaporation of the solution in alcohol of the substance. They are rod-like in appearance. The

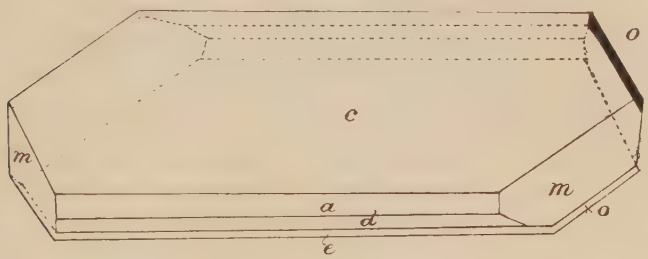
* Communicated by Sir W. H. Bragg, K.B.E., F.R.S.

† *Zeit. Phys. Chem.* xcix. p. 242 (1921).

‡ 'X-rays and Crystal Structure,' 5th edition, p. 251.

c (001) face is a flat face ; other predominant faces observed are *d* (201) and *m* (110). In some crystals faces *k* (021), *o* (11$\bar{1}$), and *e* (40$\bar{3}$) are also present. The shape of the crystal is shown in fig. 1.

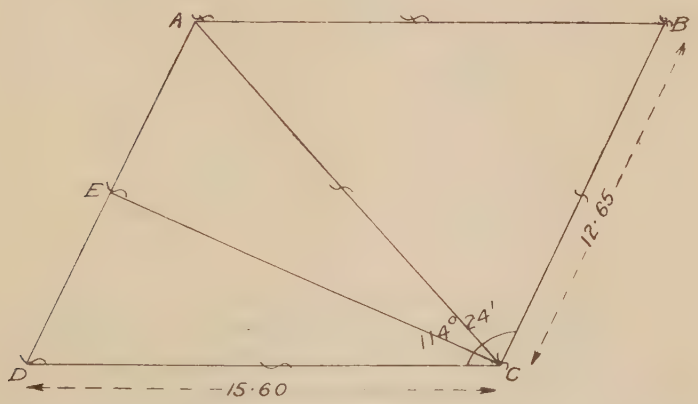
Fig. 1.



The crystallographic measurements of the crystals indicate that they belong to the monoclinic prismatic class. The axial ratio found by crystallographers is

$$a : b : c = 2{\cdot}1076 : 1 : 1{\cdot}3312\ *.$$

Fig. 2.



In the present investigation the crystals were examined by the rotating crystal method. With a Shearer gas-tube containing an anti-cathode made of copper the rotation photographs about the three axes were taken ; the dimensions of the cell were found to be (see fig. 2).

$a = 12{\cdot}65$ Å., $b = 6{\cdot}06$ Å., $c = 15{\cdot}60$ Å., and $\beta = 114°\ 24'$.

* *Cf.* Groth, *Chemische Krystallographie*, v. p. 60.

The axial ratios are

$$a : b : c = 2{\cdot}087 : 1 : 2{\cdot}574.$$

The c axis is twice that found by Becker and Jancke.

The crystals of azobenzene are volatile ; on exposure to air they become smaller ; and the setting was often spoiled during the time of exposure ; hence considerable difficulty was found in taking good rotation photographs. But with a Shearer's tube well set it was found that a good rotation photograph could be taken in about 15 minutes and an oscillation photograph in about 8–10 minutes.

In order to examine further the doubling of the c axis, and to compare the intensity of reflexion from various planes, the oscillation photographs about the a and b axes were taken in as short a time as possible. The indices of the spots appearing on the plate were worked out by means of Bernal's method of analysis *. The following tables give the indices of the planes observed, together with a rough idea of their relative intensities. The method adopted in estimating the intensity of the spot was that used by Robertson †, *i. e.*, by comparing the Kα (copper) reflexion spot of weaker planes with the Kβ reflexions of the stronger planes. The symbols used carry the same meaning as in Robertson's paper †, and are repeated here for the sake of clearness.

v.s. =very strong.	w.m. =weak medium.
s. =strong.	w. =weak.
m.s. =medium strong.	v.w. =very weak.
m. =medium.	

It will be seen from the nature of reflexions from planes (*ool*) that they are very weak when l is odd : probably the error in Becker and Jancke's determination of the c axis arose on this account. The plane (001) observed in the oscillation photograph about the b axis was much weaker than the β spot of the plane(002), which was very strong.

Table I. shows that the planes (*hol*) are halved when h is odd and there are no other general halvings. This halving corresponds to the space-group C_{2h}^{4} or C_{2h}^{5} with $\bar{m}$ lattice. The space-group C_{2h}^{5} requires that, in addition

* Proc. Roy. Soc. A, cxiii. p. 117 (1926).
† Proc. Roy. Soc. A, cxviii. p. 712 (1928).

to the halving mentioned above, the planes (010) should also be halved. It is probable in this case that the plane (010) is halved and that (020) is a very weak plane, and hence did not appear; the space-group therefore is C_{2h}^5. This probability is the greater because crystals of tolane, which is isomorphous with azobenzene, have been examined by Miss K. Yardley by the ionization spectrometer and the plane (010) has been found to be halved. The author is much indebted to Miss Yardley for supplying him with her data on tolane. The author has examined tolane by the photographic method, and the results of this

TABLE I.

Axial planes.	Planes (*hol*).		Planes (*okl*).	Planes (*hko*).
001 w.	201 v.s.	402 s.	011 m.s.	110 v.s.
002 v.s.	202 v.s.	403 s.	012 v.s.	120 w.m.
003 w.	203 v.s.	404 s.	013 s.	130 m.
004 v.s.	204 v.w.	405 v.w.	014 s.	220 m.
005 v.w.	205 v.w.	$40\bar{1}$ w.m.	015 v.w.	320 m.
006 m.	206 m.	$40\bar{2}$ s.	016 w.	420 m.s.
007 v.w.	207 m.	$40\bar{3}$ m.	017 v.w.	520 w.
008 w.m.	$20\bar{2}$ v.s.	$40\bar{6}$ s.	018 v.w.	210 m.
200 v.s.	$20\bar{3}$ v.s.	$40\bar{7}$ m.s.	021 w.	310 w.m.
	$20\bar{4}$ v.s.	$40\bar{8}$ s.	022 w.m.	410 s.
	$20\bar{5}$ v.s.	$40\bar{9}$ m.	023 w.	230 w.m.
	$20\bar{6}$ v.w.	$60\bar{4}$ w.	024 v.w.	330 w.m.
	$20\bar{7}$ v.w.		025 v.w.	
	$20\bar{8}$ m.		026 v.w.	
			031 v.w.	

investigation will shortly be communicated in another paper.

The number of molecules in the unit cell required by the space-group C_{2h}^5 is four. The number of molecules calculated from the dimensions of the cell and the density of the crystals being also four, the molecules in the cell are asymmetric. The elements of symmetry of the cell are, in accordance with the space-group, a glide plane of symmetry parallel to the (*ac*) plane and screw-axes parallel to the *b* axis *.

* *Cf.* Astbury and Yardley, Phil. Trans. A, ccxxiv. pp. 221–257.

Table II.

Planes (*hkl*).

$11\bar{1}$ s.	$12\bar{1}$ w.m.	$21\bar{1}$ v.s.	$22\bar{1}$ s.	$31\bar{1}$ s.	$32\bar{1}$ s.	$41\bar{1}$ m.	$42\bar{1}$ w.m.
$11\bar{2}$ v.s.	$12\bar{2}$ w.m.	$21\bar{2}$ m.s.	$22\bar{2}$ w.m.	$31\bar{2}$ s.	$32\bar{2}$ w.	412 s.	$42\bar{2}$ w.
$11\bar{3}$ v.s.	$12\bar{3}$ w.m.	$21\bar{3}$ m.s.	$22\bar{3}$ m.	$31\bar{3}$ w.m.	$32\bar{3}$ w.m.	$41\bar{3}$ w.m.	$42\bar{3}$ w.m.
$11\bar{4}$ v.s.	$12\bar{4}$ w.m.	$21\bar{4}$ m.s.	$22\bar{4}$ m.	$31\bar{4}$ m.s.	$32\bar{4}$ m.	$41\bar{4}$ v.w.	$42\bar{4}$ m.
$11\bar{5}$ m.s.	$12\bar{5}$ w.	$21\bar{5}$ m.s.	$22\bar{5}$ w.m.	$31\bar{5}$ w.	$32\bar{5}$ w.	$41\bar{5}$ w.	$42\bar{5}$ w.
$11\bar{6}$ m.	$12\bar{6}$ w.m.	216 m.s.	$22\bar{6}$ w.m.	$31\bar{6}$ w.m.	$32\bar{6}$ w.	416 m.	$42\bar{7}$ v.w.
$11\bar{7}$ v.w.	$12\bar{7}$ v.w.	$21\bar{7}$ w.	$22\bar{7}$ w.m.	$31\bar{7}$ m.s.	$32\bar{7}$ v.w.	$41\bar{7}$ m.	421 v.w.
$11\bar{8}$ v.w.	$13\bar{3}$ w.m.	$21\bar{8}$ v.w.	$23\bar{2}$ v.w.	$31\bar{8}$ s.	$33\bar{3}$ v.w.	$41\bar{8}$ m.	423 v.w.
111 v.s.	121 w.m.	211 m.s.	$23\bar{3}$ v.w.	$31\bar{9}$ w.m.	321 m.	$41\bar{9}$ v.w.	$51\bar{6}$ w.
112 v.s.	122 w.m.	212 v.s.	221 w.	311 w.	322 w.m.	411 w.	$61\bar{2}$ w.
113 v.s.	123 v.w.	213 m.	222 m.	312 m.	323 w.m.	412 m.	
114 m.	124 w.	214 m.s.	223 w.	313 m.	324 w.	413 m.	
115 v.w.	125 m.	215 v.w.	224 w.	314 s.		414 m.s.	
117 v.w.	132 w.m.	216 m.s.	231 v.w.	315 v.w.			
	133 v.w.			316 w.m.			

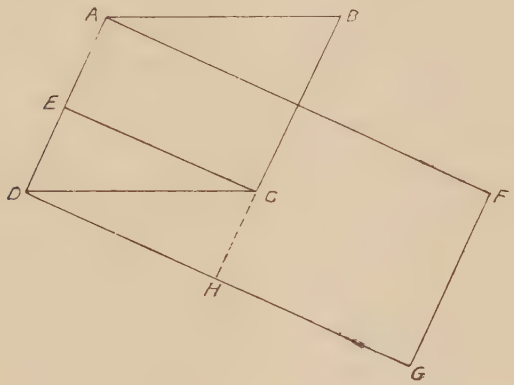
In fig. 2, if A and C are joined, the length of the side AC is 15·51 Å., which is very nearly equal to the length of the side CD. Therefore EC is nearly at right angles to AD. Hence if ADFG (fig. 3) be taken as the boundary, in the (010) plane, of a cell which will be twice as large as the unit cell, the new cell will be nearly orthogonal.

The dimensions of the cell will then be

$a=12{\cdot}65$ Å., $b=6{\cdot}06$ Å., $c=28{\cdot}4$ Å., and $\beta=90°$ (very nearly),

and the cell will contain eight molecules. The indices of the planes given in Tables I. and II. can easily be found in

Fig. 3.



terms of the new coordinates. The plane (hkl) will become $(h'k'l')$, where

$$h'=h,$$
$$k'=k,$$
and $$l'=2l+h.$$

It is then interesting to find, as the following tables show, that $(h'k'l')$ and $(h'k'\bar{l}')$ have not only the same spacings, very nearly, but also correspond similarly in regard to intensities.

It is fairly safe to infer that the molecule of azobenzene lies so that its long dimension is generally parallel to one of the coordinate axes. It is somewhat premature to attempt other deductions until the reflexions have been measured not only relatively but absolutely. This ex-

tension of the investigation will be carried out as soon as possible.

In conclusion, I wish to express my sincere thanks to Sir William Bragg, F.R.S., for suggesting the work and taking a great interest in the investigation. My thanks are also due to Dr. Shearer and Dr. Muller for guidance in the technique of X-ray methods as applied to crystal structure; to Mr. Bernal for giving me helpful and valuable suggestions from time to time; and to the authorities of the Royal Institution, who gave me the opportunity to carry on this investigation.

TABLE III.

Axial planes.	(*hol*) planes.	
002 w.	202 v.s.	$20\bar{2}$ v.s.
004 v.s.	204 v.s.	$20\bar{4}$ v.s.
006 w.	206 v.s.	$20\bar{6}$ v.s.
008 v.s.	208 v.s.	$20\bar{8}$ v.s.
0010 v.w.	2010 v.w.	$20\bar{1}0$ v.w.
0012 m.	2012 v.w.	$20\bar{1}2$ v.w.
0014 v.w.	2014 m.	$20\bar{1}4$ m.
0016 w.m.	2016 m.	
(012) m.s.	400 s.	
(014) v.s.	402 w.m.	$40\bar{2}$ m.
(016) s.	408 s.	$40\bar{8}$ s.
(018) s.	4010 s.	$40\bar{1}0$ m.s.
(0110) v.w.	4012 s.	$40\bar{1}2$ s.
(0112) w.	4014 v.w.	$40\bar{1}4$ m.
(0114) v.w.		$60\bar{2}$ w.
(0116) v.w.		
022 w.		
024 w.m.		
026 w.		
028 v.w.		
0210 v.w.		
0212 v.w.		
032 v.w.		

Summary.

The structure of the azobenzene crystal has been examined. The dimensions of the unit cell are

$a = 12{\cdot}65$ A.U.; $b = 6{\cdot}06$ A.U.; $c = 15{\cdot}60$ A.U.; $\beta = 114^\circ 24'$

TABLE IV.

Other Planes.

111 v.s.	$11\bar{1}$ s.	210 v.s.	
113 v.s.	$11\bar{3}$ v.s.	212 m.	$21\bar{2}$ m.s.
115 v.s.	$11\bar{5}$ v.s.	214 m.s.	$21\bar{4}$ m.s.
117 v.s.	$11\bar{7}$ v.s.	216 v.s.	$21\bar{6}$ m.s.
119 m.	$11\bar{9}$ m.s.	218 m.	$21\bar{8}$ m.s.
1111 v.w.	$111\bar{1}$ m.	2110 m.s.	$21\bar{1}0$ m.s.
	$111\bar{3}$ v.w.	2112 v.w.	$21\bar{1}2$ w.
1115 v.w.	$111\bar{5}$ v.w.	2114 m.s.	$21\bar{1}4$ v.w.
121 w.m.	$12\bar{1}$ w.m.	220 s.	
123 w.m.	$12\bar{3}$ w.m.	222 m.	$22\bar{2}$ w.m.
125 w.m.	$12\bar{5}$ w.m.	224 w.	$22\bar{4}$ m.
127 v.w.	$12\bar{7}$ w.m.	226 m.	$22\bar{6}$ m.
129 w.	$12\bar{9}$ w.	228 w.	$22\bar{8}$ w.
1211 m.	$121\bar{1}$ w.m.	2210 w.	$22\bar{1}0$ w.m.
	$121\bar{3}$ v.w.		$22\bar{1}2$ w.m.
131 m.		232 w.m.	$23\bar{2}$ v.w.
135 w.m.	$13\bar{5}$ w.m.	234 v.w.	$23\bar{4}$ v.w.
137 v.w.		410 s.	
311 s.	$31\bar{1}$ s.	412 m.	$41\bar{2}$ w.m.
313 w.m.	$31\bar{3}$ w.m.	414 s.	$41\bar{4}$ v.w.
315 w.	$31\bar{5}$ m.s.	416 w.	$41\bar{6}$ w.
317 m.	$31\bar{7}$ w.	418 m.	$41\bar{8}$ m.
319 m.	$31\bar{9}$ w.m.	4110 m.	$41\bar{1}0$ m.
3111 s.	$311\bar{1}$ m.s.	4112 m.s.	$41\bar{1}2$ m.
3113 v.w.	$311\bar{3}$ s.		$41\bar{1}4$ v.w.
3115 w.m.	$311\bar{5}$ w.m.	420 w.	
321 s.	$32\bar{1}$ w.	422 w.m.	$42\bar{2}$ w.m.
323 m.	$32\bar{3}$ w.m.	424 m.s.	$42\bar{4}$ m.
325 m.	$32\bar{5}$ m.	426 v.w.	$42\bar{6}$ w.
327 w.m.	$32\bar{7}$ w.	4210 v.w.	$42\bar{1}0$ v.w.
329 w.m.	$32\bar{9}$ w.	517 w.	
3211 w.	$321\bar{1}$ v.w.	525 w.	612 w.
333 w.m.	$33\bar{3}$ v.w.		

The cell contains four molecules. A remarkable feature is the nearly complete symmetry about the $(20\bar{1})$ plane, both in respect to the geometrical relations and to the intensities of reflexion by corresponding planes.

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XXVI. *Three-Dimensional Periodic Orbits in the Field of a Non-Neutral Dipole.* *By* Leigh Page *.

Abstract.

(1) The periodic orbits of an electron moving in the field of a stationary electric doublet which has a positive charge associated with it are investigated by the Newtonian dynamics.

(2) Special cases of orbits on a cone and orbits on a sphere are treated.

(3) The Hamilton-Jacobi method is applied to the problem, the energy being expressed as a function of the phase integrals. The motion is shown to be completely non-degenerate.

THE two dimensional periodic orbits of an electron in a plane through the axis of a stationary electric dipole have been investigated by D. Wrinch † and M. A. Higab ‡. The first author considers the case of a neutral dipole and shows that the only periodic orbit is a semi-circle in which the angle θ made by the radius vector with the axis of the doublet oscillates between the values $-\pi/2$ and $\pi/2$. The second author treats the more general case of a doublet which has associated with it a positive charge, and finds orbits which surround the doublet (in particular, circular orbits) as well as orbits which do not.

The object of the present contribution is to discuss the three-dimensional periodic orbits of an electron in the field of an electrical doublet of moment $m\lambda/e$ with which is associated a positive charge $m\mu/e$, m and e representing the mass and charge respectively of the electron.

Using polar coordinates r, θ, ϕ, where θ is the angle which the radius vector makes with the axis of the dipole and ϕ the azimuth, the equations of motion are

$$\ddot{r} - r\dot{\theta}^2 - r\sin^2\theta\dot{\phi}^2 = -\frac{\mu}{r^2} - \frac{2\lambda\cos\theta}{r^3}, \quad . \quad . \quad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta}) - r\sin\theta\cos\theta\dot{\phi}^2 = -\frac{\lambda\sin\theta}{r^3}, \quad . \quad . \quad (2)$$

$$\frac{1}{r\sin\theta}\frac{d}{dt}(r^2\sin^2\theta\dot{\phi}) = 0. \quad . \quad . \quad . \quad . \quad (3)$$

* Communicated by the Author.

† Phil. Mag. xliii. p. 993 (1923).

‡ *Ibid.* vii. p. 783 (1929).

Integrating (3)

$$r^2 \sin^2\theta\dot{\phi} = h, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and using (4) to eliminate $\dot{\phi}$ from (2) the latter equation can be integrated, giving

$$r^4\dot{\theta}^2 = a^2 + 2\lambda\cos\theta - \frac{h^2}{\sin^2\theta}. \quad . \quad . \quad . \quad (5)$$

Next ϕ and θ may be eliminated from (1) by means of (4) and (5), and the resulting equation integrated. This gives

$$\dot{r}^2 = -2w + \frac{2\mu}{r} - \frac{a^2}{r^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The constants μ, λ, h, a, w have the following physical dimensions :—

$$\mu = \frac{L^3}{T^2}, \quad \lambda = \frac{L^4}{T^2}, \quad a = h = \frac{L^2}{T}, \quad w = \frac{L^2}{T^2}.$$

From (4) it is clear that h represents the azimuthal momentum per unit mass. To find the significance of w we form the energy equation from (4), (5), (6) :

$$\tfrac{1}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2) - \frac{\mu}{r} - \frac{\lambda\cos\theta}{r^2} = -w. \quad . \quad (7)$$

Evidently w is the negative of the total energy per unit mass. Periodic orbits are possible only for positive values of w. It will be shown later that a^2 must be positive as well.

Equations of the Orbit.

We can describe the orbit in the general case as the curve of intersection of two surfaces

$$F(r, \theta) = 0, \qquad G(\theta, \phi) = 0.$$

To obtain the first put $u \equiv 1/r$, $x \equiv \cos\theta$, and eliminate the time between (5) and (6). We find

$$\frac{-du}{\sqrt{-2w + 2\mu u - a^2u^2}} = \frac{dx}{\sqrt{2\lambda f(x)}}, \quad . \quad . \quad . \quad (8)$$

where

$$f(x) \equiv \left(\frac{a^2}{2\lambda} + x\right)(1 - x^2) - \frac{h^2}{2\lambda}. \quad . \quad . \quad . \quad (9)$$

In order that the motion in u shall be periodic, the expression under the radical on the left-hand side of

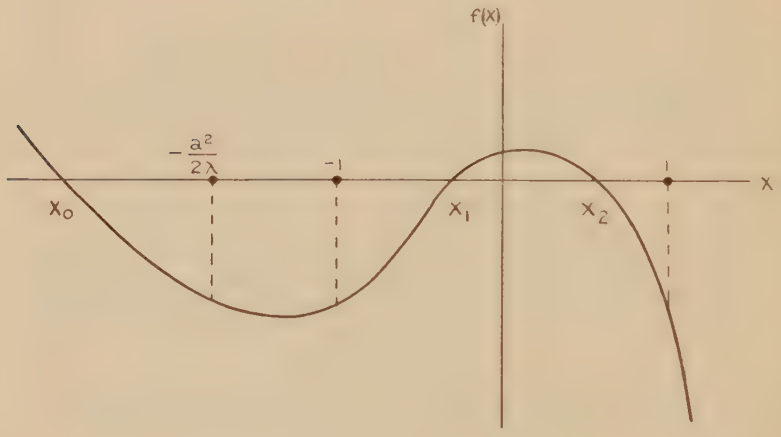
(8) must be positive only for values of u lying between two positive libration limits u_1 and u_2. Hence a^2 must be positive as well as w. The libration limits are

$$u_1 = \frac{1}{a^2}(\mu - \sqrt{\mu^2 - 2a^2 w}), \qquad u_2 = \frac{1}{a^2}(\mu + \sqrt{\mu^2 - 2a^2 w}). \quad (10)$$

For these to be real, it is necessary that $2a^2 w \leq \mu^2$, the case of equality being that in which the libration limits coincide, and the motion is therefore confined to the surface of a sphere.

For the motion in θ to be periodic the function $f(x)$ must be positive for values of x lying between two real roots x_1 and x_2 which satisfy the conditions

$$-1 \leq x_1 < x_2 < 1.$$



These roots mark the extreme values which $\cos\theta$ is capable of assuming.

We note that

$$f(-\infty) = \infty, \quad f\left(-\frac{a^2}{2\lambda}\right) = f(-1) = f(1) = -\frac{h^2}{2\lambda},$$

$$f(\infty) = -\infty.$$

Therefore $f(x)$ has one real root x_0 less than the smaller of the two quantities $-a^2/2\lambda$ and -1. If the other roots are real so that the motion is physically possible, the graph of the function is as indicated in the figure.

The function $f(x)$ is a maximum for

$$x_m = \frac{1}{6\lambda}(\sqrt{a^4+12\lambda^2}-a^2), \quad . \quad . \quad . \quad (11)$$

which is always positive and less than unity. If the function vanishes at its maximum x_1 and x_2 coincide, and the motion is limited to the surface of a circular cone. It is clear from (9) that for any admissible values of a^2 and λ the roots x_1 and x_2 are real and within the prescribed limits for all values of h ranging in absolute value from 0 up to a maximum

$$h_m = 2\lambda\left\{\left(\frac{a^2}{2\lambda}+x_m\right)(1-x_m{}^2)\right\}^{\frac{1}{2}}.$$

If λ is small, approximate values of the roots are

$$x_0 = -\frac{a^2}{2\lambda}\left(1+4\lambda^2\frac{h^2}{a^6}\ldots\right),$$

$$x_1 = -\sqrt{1-\frac{h^2}{a^2}}+\lambda\frac{h^2}{a^4}+2\lambda^2\frac{h^2}{a^6}\frac{1-\frac{5}{4}\frac{h^2}{a^2}}{\sqrt{1-\frac{h^2}{a^2}}}\ldots, \quad (12)$$

$$x_2 = \sqrt{1-\frac{h^2}{a^2}}+\lambda\frac{h^2}{a^4}-2\lambda^2\frac{h^2}{a^6}\frac{1-\frac{5}{4}\frac{h^2}{a^2}}{\sqrt{1-\frac{h^2}{a^2}}}\ldots$$

Let us put

$$v \equiv u-\frac{u_1+u_2}{2}, \qquad b \equiv \frac{u_2-u_1}{2};$$

$$y \equiv x-\frac{x_1+x_2}{2}, \qquad -y_0 \equiv x_0-\frac{x_1+x_2}{2}, \qquad c \equiv \frac{x_2-x_1}{2};$$

b and c representing the amplitudes of u and x respectively. Then the integral of (8) is

$$\alpha-\sin^{-1}\frac{v}{b} = \frac{a}{\sqrt{2\gamma y_0}}\left[\left(1+\frac{3}{16}\frac{c^2}{y_0{}^2}\ldots\right)\sin^{-1}\frac{y}{c}\right.$$
$$\left.+\left(1-\frac{3}{8}\frac{y}{y_0}\ldots\right)\frac{\sqrt{c^2-y^2}}{2y_0}\right], \quad . \quad (13)$$

where α is a constant of integration.

To get the relation between θ and ϕ we eliminate r and t between (4) and (5). This gives

$$d\phi = \frac{h\,dx}{(1-x^2)\sqrt{2\lambda f(x)}}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Integrating we have

$$\phi - \phi_0 = \frac{h}{\sqrt{8\lambda y_0}} \left\{ \left[1 + \frac{1}{2}\frac{1+\bar{x}}{y_0} + \frac{3}{8}\frac{(1+\bar{x})^2}{y_0^2} \cdots \right] \right.$$
$$\times \frac{1}{\sqrt{(1+\bar{x})^2 - c^2}} \sin^{-1} \left\{ \frac{1+x}{c} - \frac{(1+\bar{x})^2 - c^2}{c(1+x+y)} \right\}$$
$$+ \left[1 - \frac{1}{2}\frac{1-\bar{x}}{y_0} + \frac{3}{8}\frac{(1-\bar{x})^2}{y_0^2} \cdots \right] \frac{1}{\sqrt{(1-\bar{x})^2 - c^2}}$$
$$\left. \sin^{-1} \left\{ \frac{(1-\bar{x})^2 - c^2}{c(1-x-y)} - \frac{1-x}{c} \right\} - \frac{3}{4y_0^2} \sin^{-1}\frac{y}{c} \cdots \right\}, \quad (15)$$

where $\bar{x} \equiv (x_1 + x_2)/2$.

The period P_r of r is obtained at once from (6). We have

$$P_r = \oint \frac{dr}{\sqrt{-2w + \frac{2\mu}{r} - \frac{a^2}{r^2}}} = \frac{2\pi\mu}{(2w)^{\frac{3}{2}}}. \quad . \quad (16)$$

Certain special types of motion are of interest. These may be classified as follows :—

(a) ϕ constant. The motion is limited to a plane through the axis of the dipole. This case has been discussed in detail by Higab (*loc. cit.*).

(b) θ constant. The orbit lies on the surface of a right circular cone whose axis coincides with the axis of the dipole.

(c) r constant. The motion is confined to the surface of a sphere. Cases (b) and (c) will now be investigated in detail.

Motion on the Surface of a Cone.

For this type of motion the roots x_1 and x_2 of $f(x)$ coincide with the value (11) for which the function is a maximum. So the angle of the cone is given by

$$\cos\theta = x = \frac{1}{6\lambda}(\sqrt{a^4 + 12\lambda^3} - a^2), \quad . \quad . \quad (17)$$

for a specified value of a. Solving for a^2 and determining h from (9)

$$a^2 = \lambda\frac{1-3x^2}{x}, \qquad h^2 = \frac{\lambda}{x}(1-x^2)^2. \quad . \quad . \quad (18)$$

As a^2 must be positive and both a^2 and h^2 finite,

$$\cos^{-1}\frac{1}{\sqrt{3}} \leqslant \theta < \frac{\pi}{2}.$$

Consequently the angle θ of the cone must lie between 54°·8 and 90°.

Eliminating the time between (4) and (6) the differential equation of the orbit is found to be

$$\frac{-du}{\sqrt{-2w+2\mu u^2-a^2u^2}} = \frac{\sin^2\theta}{h}d\phi, \quad . \quad . \quad (19)$$

of which the integral is

$$\frac{1}{r} = \frac{1}{a^2}\left[\mu + \sqrt{\mu^2-2a^2w}\cos\left\{\sqrt{1-3\cos^2\theta}(\phi-\phi_0)\right\}\right], \quad (20)$$

where

$$a^2 = \lambda\frac{1-3\cos^2\theta}{\cos\theta}, \qquad w \leqslant \frac{\mu^2}{2a^2}.$$

This is the equation of an ellipse with rotating apsides inscribed on the surface of the cone, the focus being at the origin. If we develop the cone on a plane, using the polar coordinates r and α,

$$\alpha = \phi\sin\theta,$$

and the equation of the developed orbit is

$$\frac{1}{r} = \frac{1}{a^2}\left[\mu + \sqrt{\mu^2-2a^2w}\cos\left\{(\sin\theta)^{-1}\sqrt{1-3\cos^2\theta}(\alpha-\alpha_0)\right\}\right]$$
$$. \quad . \quad . \quad (21)$$

The semi-major axis A of the ellipse is $\mu/2w$ and the period of r is

$$P_r = 2\pi\frac{A^{3/2}}{\sqrt{\mu}},$$

which is identical with Kepler's third law of planetary motion.

The mean period of revolution is evidently

$$P_\phi = P_r\sqrt{1-3\cos^2\theta}, \quad . \quad . \quad . \quad . \quad (22)$$

so $P_\phi < P_r$ for all admissible values of θ.

As an example of motion on the surface of cone assume $\mu = 10$, $\lambda = 8$, $\theta = 60°$. Then $h = 3$, $a = 2$, and taking $w = 4{\cdot}5$,

$$\frac{1}{r} = 2{\cdot}5 + 2\cos\tfrac{1}{2}(\phi-\phi_0),$$

the radius vector oscillating between the minimum value 2/9 and the maximum 2. For r to go through a cycle of values two revolutions are necessary. The periods are

$$P_r = \frac{20\pi}{27}, \qquad P_\phi = \frac{10\pi}{27}.$$

The pseudo-elliptical orbit degenerates into a circle under the following circumstances :—

$$(1) \quad w = \frac{\mu^2}{2a^2} = \frac{\mu^2}{2\lambda}\frac{\cos\theta}{1-3\cos^2\theta}.$$

The orbit is a circle of radius

$$r = \frac{\lambda}{\mu}\frac{1-3\cos^2\theta}{\cos\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

For each admissible value of θ there is one and only one circular orbit, the radius of the circle increasing from 0 to ∞ as θ varies from 54°·8 to 90°. For a given θ the period P_ϕ is less for the circular orbit than for any other orbit. If w has its maximum value 12·5 in the numerical example cited above, the orbit is a circle of radius 0·4 and period $2\pi/25$.

$$(2) \quad \mu = 0.$$

In this case θ can be only $\cos^{-1}\frac{1}{\sqrt{3}}$, but the radius of the circle may have any value. No other type of periodic orbit on the surface of a cone is possible under this condition. The period P_ϕ is

$$P_\phi = \frac{2\pi r^2}{3^{1/4}\sqrt{\lambda}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Motion on the Surface of a Sphere.

For the motion to take place on the surface of a sphere u_1 must equal u_2. Therefore $2a^2w = \mu^2$ and

$$r = \frac{1}{u} = \frac{a^2}{\mu} = \frac{\mu}{2w}, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

showing that this type of motion is impossible if $\mu = 0$ except for the circular orbit previously considered.

The equation of the orbit is given in differential form by (14) and in integrated form by (15), $\cos\theta$ oscillating between the roots x_1 and x_2 of $f(x)$ as the electron progresses around the axis of the doublet. The motion is similar to that of the apex of a top acted on by the torque due

to gravity, although retrograde motion is impossible, since it is clear from (4) that for h not equal to zero $\dot{\phi}$ can never vanish or change sign. Consequently the orbit always meets the limiting parallels of latitude tangentially. Since $x_1+x_2>0$ it follows from (4) that the revolution is more rapid when θ is minimum than when θ is maximum.

The period of θ is obtained at once from (5). It is

$$P_\theta = \frac{r^2}{\sqrt{2\lambda}} \oint \frac{dx}{f(x)}$$

$$= \frac{2\pi r^2}{\sqrt{2\lambda y_0}} \left(1 + \frac{3}{16}\frac{c^2}{y_0^2} \cdots\right). \quad . \quad . \quad . \quad (26)$$

Substituting the approximate values of the roots given by (12) and using (25)

$$P_\theta = \frac{2\pi\mu}{(2w)^{3/2}} \left\{1 + 3\frac{\lambda^2 w^2}{\mu^4}\left(1 - 10\frac{wh^2}{\mu^2}\right) \cdots\right\}$$

$$= \frac{2\pi r^{3/2}}{\sqrt{\mu}} \left\{1 + \frac{3}{4}\frac{\lambda^2}{\mu^2 r^2}\left(1 - 5\frac{h^2}{\mu r}\right) \cdots\right\}. \quad . \quad (27)$$

When θ goes through a cycle of values we see from (15) that ϕ increases by

$$\Delta\phi = \frac{\pi h}{\sqrt{2\lambda y_0}} \left\{\frac{1}{\sqrt{(1+\bar{x})^2 - c^2}} \left[1 + \frac{1}{2}\frac{1+\bar{x}}{y_0} + \frac{3}{8}\frac{(1+\bar{x})^2}{y_0^2} \cdots\right]\right.$$

$$\left. + \frac{1}{\sqrt{(1-\bar{x})^2 - c^2}} \left[1 - \frac{1}{2}\frac{1-\bar{x}}{y_0} + \frac{3}{8}\frac{(1-\bar{x})^2}{y_0^2} \cdots\right] - \frac{3}{4y_0^2} \cdots\right\}$$

$$. \quad . \quad . \quad (28)$$

The mean azimuthal angular velocity is then

$$\bar{\dot{\phi}} = \frac{\Delta\phi}{P_\theta}.$$

In terms of the approximate values of the roots (12)

$$\bar{\dot{\phi}} = \frac{\sqrt{\mu}}{r^{3/2}} \left\{1 - \frac{3}{4}\frac{\lambda^2}{\mu^2 r^2}\left(1 + 2\frac{h}{\sqrt{\mu r}} - 5\frac{h^2}{\mu r}\right) \cdots\right\}. \quad (29)$$

Therefore the mean period of revolution P_ϕ is related to P_θ by the equation

$$P_\phi = P_\theta \left\{1 + \frac{3}{2}\frac{\lambda^2 h}{(\mu r)^{5/2}} \cdots\right\}, \quad . \quad . \quad . \quad (30)$$

indicating that $P_\phi > P_\theta$.

To illustrate this type of motion take $\mu = 10$, $\lambda = 8$ as before, and let $h^2 = 24$, $w = 50/24$. Then $r = 2{\cdot}4$, $a^2 = 24$, and

$$f(x) = -x^3 - \tfrac{3}{2}x^2 + x = -x(x - \tfrac{1}{2})(x + 2).$$

So

$$x_0 = -2, \qquad x_1 = 0, \qquad x_2 = \tfrac{1}{2},$$

and θ oscillates from 60° to 90°. Moreover,

$$y_0 = \tfrac{9}{4}, \qquad c = \dot{x} = \tfrac{1}{4},$$

and from (26) and (30)

$$P_\theta = 6{\cdot}032(1 + {\cdot}0023 + \ldots) = 6{\cdot}046$$
$$P_\phi = 6{\cdot}046(1 + {\cdot}17 + \ldots) = 7{\cdot}1.$$

Hamilton-Jacobi Method of Solution.

The Hamilton-Jacobi equation, obtained at once from the energy equation (7), is

$$\frac{1}{2}\left\{\left(\frac{\partial S}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial S}{\partial \theta}\right)^2 + \frac{1}{r^2 \sin^2\theta}\left(\frac{\partial S}{\partial \phi}\right)^2\right\} - \frac{\mu}{r} - \frac{\lambda \cos\theta}{r^2} = -w. \quad . \quad . \quad (31)$$

The variables are easily separated and the phase integrals calculated. They are

$$I_\phi = 2\pi h,$$
$$I_\theta = 2\pi(a - h) - \frac{\pi\lambda^2}{2a^3}\left(1 - 3\frac{h^2}{a^2}\right)\ldots, \quad . \quad . \quad (32)$$
$$I_r = 2\pi\left(\frac{\mu}{\sqrt{2w}} - a\right),$$

where the constants of separation h and a have the same significance as the constants designated by the same letters in the previous treatment of the motion. Evidently h is a function of I_ϕ alone, a of I_ϕ and I_θ, and w of the three phase integrals.

If $$I \equiv I_r + I_\theta + I_\phi$$

elimination of h and a gives for the energy expressed as a function of the phase integrals

$$H = -w = -\frac{2\pi^2\mu^2}{I^2} + \frac{16\pi^6\mu^2\lambda^2}{I^8(I_\theta + I_\phi)^3}\left\{1 - 3\frac{I_\phi^2}{(I_\theta + I_\phi)^2}\right\}\ldots \quad (33)$$

up to terms in λ^4. The fundamental frequencies may be obtained by differentiating H partially with respect to the I's. The periods given in the earlier part of the paper have been checked from the frequencies so obtained. Evidently the motion for finite λ and μ is completely non-degenerate.

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November 11, 1929.

XXVII. *On Polymolecular Films.* *By* R. S. Bradley *.

SEVERAL cases are known in which a vapour adsorbs on a solid surface to give a film several layers in thickness. Lehner † obtained thick films of water on platinum, glass, and quartz. Frazer, Patrick, and Smith ‡ criticized Lehner's work on the grounds that the walls were etched by acids. They found no adsorption of toluene on a plane surface. Smits §, however, has obtained polymolecular layers of mercuric iodide on glass 500 molecules thick at 300° C., and J. W. Smith ‖ thick layers of water and benzene on amalgamated platinum (as smooth as possible). Since the range of surface forces is small, the formation of such films must be due to interaction between adsorbed molecules. In this paper interaction caused by electric polarization will be studied.

Landé and R. Lorenz ¶ have considered the case of an electric doublet forming an electrical image in a solid surface. If the dipole makes an angle θ with the normal to the surface, the energy of the doublet in the field of its electrical image is

$$\frac{-\mu^2}{2r^3}(3+\cos 2\theta),$$

where μ is the strength of the dipole and r is its distance from the surface. Adopting a treatment slightly different from Landé and Lorenz's, dN the number of mols. per c.c.

* Communicated by the Author.
† Lehner, J. C. S. 1927, p. 272.
‡ Frazer, Patrick, and Smith, J. Phys. Chem. xxxi. p. 897 (1927).
§ Smits, J. C. S. 1928, p. 2045.
‖ J. W. Smith, J. C. S. 1928, p. 2045.
¶ Landé and Lorenz, *Zeit. Anorg. Chem.* cxxv. p. 47 (1922).

at a distance r, whose axes make an angle θ with the surface normal is

$$Ce^{\frac{\mu^2}{2kTr^3}(3+\cos 2\theta)}d(\cos 2\theta).$$

Hence N_r, the number of molecules per c.c. at a distance r, is

$$N_r = Ce^{3b}\int_{-1}^{+1} e^{b\lambda}\,d\lambda,$$

where

$$b = \frac{\mu^2}{2kTr^3} \quad \text{and} \quad \lambda = \cos 2\theta.$$

Hence

$$N_r = N_\infty e^{3b}\frac{\sinh b}{b},$$

while the number of molecules adsorbed per sq. cm. is

$$\int_{a/2}^{\infty} N_\infty\left(e^{3b}\frac{\sinh b}{b} - 1\right)dr,$$

where a is the diameter of a dipole. It is clear that, instead of giving a thick film, the concentration of adsorbed molecules diminishes approximately exponentially with the distance. The calculation neglects the polarization at optical frequencies of the adsorbed molecules, and the interaction between the various adsorbed molecules and their electrical images in the surface.

The problem is, of course, a three-dimensional one. The point charges should be replaced by a Fourier development after the method of Ewald. Such a method has been applied by Kornfeld* to determine the energy of a dipole lattice. The thick film may be replaced by a static model of a dipole lattice with a fading polarization from the surface upwards. This, however, makes the calculation extremely difficult, and in this paper only the case of a dipole chain will be considered.

The dipole next to the surface is taken as completely oriented by the surface forces, and of fixed net permanent moment independent of temperature. Built up on this is a dipole chain. Each dipole forms an induced charge on the surface, which acts in the case of a conductor as if it were the mirror image of the dipole. For a dielectric of constant K the image has a moment

$$\mu\left(\frac{K-1}{K+1}\right).$$

* *Zeit. für Physik*, xxii. p. 27 (1924).

Consider n dipoles of diameter a. Let the force on the pth dipole be F_p, let μ_s be the net moment of the sth dipole, and α the polarizability.

Then

$$F_p - \sum_{s=1}^{s=p-1}\left[\frac{2\mu_s}{(p-s)^3a^3} + \frac{2\mu_s}{(p+s-1)^3a^3}\right]$$

$$+ \sum_{s=p+1}^{s=n}\left[\frac{2\mu_s}{(s-p)^3a^3} + \frac{2\mu_s}{(p+s-1)^3a^3}\right] + \frac{2\mu_p}{(2p-1)^3a^3} = 0.$$

Here the terms containing $p+s-1$ are due to the images in the conductor. Also

$$\mu_s = \mu L\left(\frac{\mu F_s}{kT}\right) + \alpha F_s,$$

where $L(x)$ is the Langevin function

$$= \coth x - \frac{1}{x} = \frac{x}{3} - \frac{x^3}{45} \quad \text{for small } x,$$

$$= 1 - \frac{1}{x} + 2e^{-2x} \quad \text{for large } x.$$

We shall take the case

$$\frac{\mu F}{kT} > 1,$$

and use the second expansion. Hence,

$$F_p - \sum_{s=2}^{s=p-1}\frac{1}{a^3}\left[\frac{1}{(p-s)^3} + \frac{1}{(p+s-1)^3}\right]$$

$$\left[2\mu\left(1 - \frac{kT}{\mu F_s}\right) + \lambda\alpha F_s\right]$$

$$- \sum_{s=p+1}^{s=n}\frac{1}{a^3}\left[\frac{1}{(s-p)^3} + \frac{1}{(p+s-1)^3}\right]$$

$$\left[2\mu\left(1 - \frac{kT}{\mu F_s}\right) + \lambda\alpha F_s\right]$$

$$- \frac{1}{(2p-1)^3a^3}\left[2\mu\left(1 - \frac{kT}{\mu F_p}\right) + \lambda\alpha F_p\right]$$

$$- \frac{2\mu + 2\alpha F_1}{a^3}\left(\frac{1}{(p-1)^3} + \frac{1}{p^3}\right) = 0.$$

It is useful to note that

$$\frac{1}{1^3}+\frac{1}{2^3}+\frac{1}{3^3}\cdots\frac{1}{x^3}=1{\cdot}202-\frac{1}{2x^2}+\frac{1}{2x^3}-\frac{1}{4x^4}\cdots$$

These n equations determine the n unknowns F. They become linear when, as a first approximation, $1-\frac{kT}{\mu F}$ is written as 1. Hence the first approximation is

$$F_p=\frac{\Delta_p}{\Delta},$$

where Δ is the determinant formed by the coefficients of the F's on the left-hand side, and Δ_p is the determinant formed by replacing the coefficients of F_p in Δ by the constants terms of each linear equation

$$AF_p+BF_1+CF_3+\ldots=\text{constant}.$$

The second approximation is then obtained by giving $1-\frac{kT}{\mu F_p}$ the values $1-\frac{kT\Delta}{\mu\Delta_p}$, giving

$$F_p=\frac{\Delta'_p}{\Delta'}.$$

The energy of the pth dipole is then

$$-\mu F_p L\left(\frac{\mu F_p}{kT}\right)-\tfrac{1}{2}\alpha F_p^2+\frac{2\lambda}{(n-1)a^{n-1}}.$$

The last term is due to the repulsive forces, and acts merely between adjacent dipoles. Its evaluation is uncertain, but it may be computed for water (the example chosen below) from Lennard-Jones' forces constants for neon * on the assumption of a neon-like sheath for the pseudo-atom water, and it is relatively small.

The solution of the determinants is laborious, and we shall consider only the case of three layers. We take a for the liquid film to be the same as for water, where X-ray diffraction suggests a similar partial orientation; $\mu=1{\cdot}7\ 10^{-18}$ and the molecular refraction $=3{\cdot}7$. The difference between the total energies of chains of three and two molecules will give the energy required to remove the surface molecule from a chain of three molecules, and this is the latent heat of evaporation, per molecule, of a film of three molecules.

* Lennard-Jones, P. R. S. cix. p. 476 (1925).

In the case of water at 25° C. we find for a layer of three molecules (E.S.U.)

$$F_3 = 1{\cdot}61\ 10^5, \quad F_2 = 2{\cdot}85\ 10^5, \quad F_1 = 3{\cdot}13\ 10^5;$$

whilst for a layer of two molecules

$$F_2 = 1{\cdot}625\ 10^5, \quad F_1 = 2{\cdot}69\ 10^5.$$

This gives for the latent heat of evaporation of the film of three molecules the value 8,600 cals. per gram mol., which agrees well with Lehner's figures for

$$\frac{-R d \log_e P_\phi}{d\left(\frac{1}{T}\right)} = L_\phi,$$

ϕ being the number of layers, viz.,

at 25° C. $\phi = 5$, $L = 9100$,
$\phi = 10$, $L = 10{,}530$.

The University, Leeds.
April 1930.

XXVIII. *Automatic Recording Waterproof Tester.*

By A. L. Hodges *.

SOME few years ago the writer had to develop a device that would record accurately the time it took water to seep through various fabrics and papers. The result was a very satisfactory piece of apparatus which is shown in the accompanying drawing.

In comparing samples for waterproof qualities it was found absolutely necessary to condition them all alike before testing. The conditioning used by the writer was to confine the samples in a space at laboratory temperature for 24 hours with a vessel having a free water surface.

For thin samples the large drop of water shown in fig. 1 was found to be all that was necessary. For thicker ones the water head shown in fig. 2 was used.

The operation of the device is simple. The water is placed on the sample and the clock started. When the

* Communicated by the Author.

water seeps through to the salt and wets it (a very quick process as the amount of salt is small) the electrical circuit is completed. The lamp lights up and the pen is pulled to one side. The current, however, being about an ampere, quickly dries the salt and shuts itself off. When the water seeps through again the pen, of course, repeats. In the drawing the record shows a breakdown time of five hours, and a first seepage time of two hours, a second seepage of one hour.

Thus the device is capable of showing automatically not only the breakdown time but the various successive

Fig. 2.

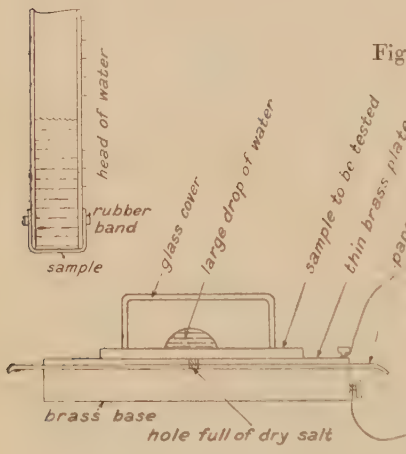
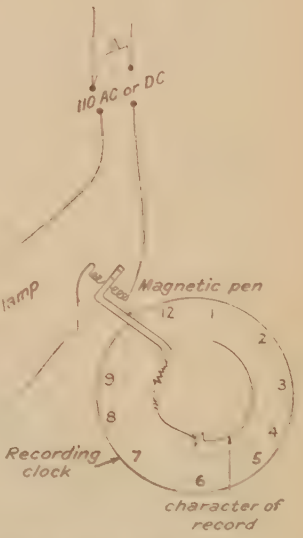


Fig. 1.



seepage times of samples. It is thought that, if the device were to come into general use, specifications and a standard scale could be arranged for it, so that the waterproof qualities of a material could be placed on a standard basis, and an understandable one. However, no attempt has so far been made to have the device manufactured, and as the materials necessary are in general available in all laboratories, it was thought that publication might result in trial by others, or at least in criticisms of value.

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XXIX *On the Absorption of X-Rays in Gases and Vapours.*—Part I. *Gases.*

By J. A. Crowther, *M.A., Sc.D., F.Inst.P., Professor of Physics in the University of Reading, and* L. H. H. Orton, *B.Sc., Wantage Scholar, University of Reading* *.

THE research described in this and subsequent papers consists in the measurement of the absorption of X-rays in a number of gases and vapours, and of the ionization produced by this absorption. A similar series of experiments was made by one of the writers † rather more than twenty years ago. The radiation used in the earlier experiments was the heterogeneous radiation from an ordinary X-ray tube. The absorption measurements were therefore of little real significance, and no conclusions of value as to the relation between absorption and ionization can be drawn from them. In spite of this there has been, as far as we are aware, no subsequent redetermination of these quantities on an extensive scale, though a few scattered observations have been recorded, and the values obtained in the early paper are still quoted in the standard books of tables. In the circumstances it was felt that a re-survey of the problem, using radiation of definite wave-length, was highly desirable. Accurate data are frequently required for practical purposes, and, in addition, it was hoped that some information might emerge on the interesting subject of the energy relations involved in the production of ions in gases by X-rays. The portion of the work now published deals with the measurements made on selected gases.

§1. *Experimental Details.*

Owing to the rapidity with which the absorption of X-rays varies with the wave-length, absorption measurements are only significant if made on radiation which is homogeneous to a fairly high degree. No practicable amount of "filtration" will produce a beam sufficiently homogeneous for the purpose ‡, and it is necessary to have recourse to a crystal reflexion method. In order to avoid

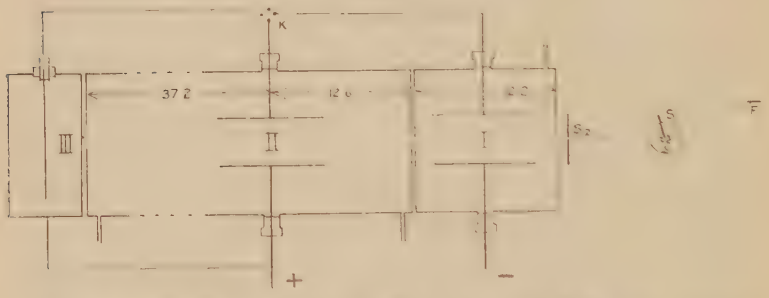
* Communicated by Prof. J. A. Crowther, Sc.D.

† J. A. Crowther, Proc. Roy. Soc. A, lxxxii. p. 103 (1909).

‡ J. A. Crowther, Brit. Journ. Rad. ii. p. 175 (1929).

too greatly attenuating the reflected beam, the crystal (a large-rock salt crystal which had been thoroughly tested in previous experiments) was mounted as shown in fig. 1, following a suggestion originally due to Seeman. A lead screen S_1 with a vertical straight edge makes contact with the vertical face of the crystal C, both screen and crystal being mounted on a turntable the axis of rotation of which coincides with the line along which the screen meets the crystal. The screen is then moved back slightly, leaving a gap of approximately one millimetre between its vertical edge and the crystal. This forms the first limiting slit of the reflected pencil; the second slit S_2, adjusted to a width of about 1 mm., is placed so that the line S_2C makes with the face of the crystal an angle equal to the glancing

Fig. 1.



angle for Cu.K_α radiation. The distance S_2C was made equal to the distance between the focal spot F of a Shearer tube fitted with a copper anticathode and the axis of rotation C, each distance being 7 cm. The preliminary settings were made optically, and the final settings by photographic methods. The arrangement had not sufficient resolving power to separate the two α components, but a photograph taken at the extreme end of the apparatus *i. e.*, 70 cm. from the crystal, showed that the radiation coming through the three chambers consisted of a well-defined beam with sharp edges and rather less than 1 mm. in width.

The Shearer tube was excited with a current of 6 ma. at a potential of 40,000 volts. Potentials of this order were required in order to produce radiation of sufficient intensity for accurate measurement. Some "general" radiation will thus be reflected to the slit S_2 in the second order

spectrum. An analysis of the radiation from the tube showed, however, that the amount of such radiation was completely negligible. As an additional test, however, the mass absorption of the radiation in aluminium was measured with the apparatus, using sheets of sufficient thickness to absorb up to $\frac{2}{3}$ of the radiation. The coefficient so obtained, 48·7, agreed closely with the value given by the recent experiments of Allen *, for the absorption of K_α radiation of copper in aluminium.

The beam after passing the slit S_2 passed axially through two cylindrical brass chambers, I. and II. (fig. 1), entering and leaving the chambers through narrow rectangular windows covered with thin cellophane of thickness 0·05 mm. Both chambers were made vacuum-tight, and could be evacuated to any desired pressure by a Hyvac pump, the pressures being measured by mercury manometers. Each chamber was fitted with a pair of parallel plate electrodes of aluminium. The collecting plate of the system was 3·8 cm. wide and was surrounded by a guard-ring of 2·5 cm. width to ensure uniformity of field across the collecting area. The distance between the electrodes was 3 cm. It was calculated that this distance was sufficient to ensure complete absorption of the photo-electrons ejected by the X-ray beam at the lowest pressures used. The final ionization chamber, III., which remained at atmospheric pressure throughout, was of the paper electrode type, investigated by Treloar †.

Chambers I. and III. always contained air. The gas under investigation was contained in chamber II. This vessel was made sufficiently long (49·8 cm.) to produce an easily measurable absorption of the radiation by the gas under observation.

Chamber I. was permanently connected to a Wilson tilted electroscope working at a sensitivity of about 100 divisions per volt. The collecting plates of II. and III. were connected to a high insulation key, so that either of them could be connected either to the electroscope or to earth. The high potential electrodes were so arranged that the charge collected by chamber I. was opposite in sign to that collected by either II. or III. The usual precautions for screening the apparatus both from stray radiation and from electrostatic disturbances were taken.

* S. J. Allen, Phys. Rev. xxviii. p. 907 (1926).

† Treloar, J. Brit. Inst. Rad. ii. p. 188 (1929).

§ 2. *Measurement of Absorption.*

All measurements were made by a balance method, originally described by one of the authors *. It has been shown that in an ionization chamber of the type of chamber I. the ionization produced by a beam of X-rays is directly proportional to the pressure of the gas in the chamber. Thus, by adjusting the pressure, it is possible to adjust the ionization current through I. to any known fraction of its value at normal atmospheric pressure. Suppose, now, that the collecting systems of I. and III. are connected to the electroscope, that of II. being earthed. Since the charges collected are opposite in sign, it will be possible to adjust the pressure in I. so that the resultant charge on the gold leaf is zero when the X-rays are passing through both chambers. The system may then be said to be balanced. Let p_1 be the pressure at which a balance is obtained when II. is evacuated, and p_1' the smaller pressure required for a balance with the chamber II. full of gas. Then $p_1 \ p_1$ is clearly the ratio of the intensities of the radiation in III. with the chamber II. full and empty, and thus measures the absorption of the column of gas. If λ is the linear coefficient of absorption for the gas $p_1' \ p_1 = \epsilon^{-d\lambda}$ where d is the length of chamber II.

This method eliminates most of the errors incidental to the measurement of small ionization currents with a sensitive electroscope. The balance is clearly independent of fluctuations in intensity of the radiation (a source of considerable uncertainty in X-ray work): it is independent of fluctuations in the sensitivity of the electroscope: and has the additional merit that slight defects in insulation do not affect the balance point, although they reduce the sensitivity of the method. In practice, with radiation of the intensity available in these experiments, it was possible to balance the system with certainty to about 1 mm. of pressure. As the smallest pressure used in I. was about 25 cm. this should give an accuracy rather better than $\frac{1}{2}$ per cent. on an individual reading.

In practice corrections have to be applied for the varying absorption of the radiation in chamber I., for the absorption of the radiation by the residual gas in II., and for the slight change in pressure in III., which being at atmospheric pressure changes with the barometer. These

* Crowther, Phil. Mag. xiv. p. 653 (1907).

corrections are of the order of a few per cent. It is also more convenient to express the results in terms of the mass absorption coefficient, μ, rather than the linear coefficient. It can easily be shown that if μ is the mass coefficient of absorption of the gas in II., and ρ its density at N.T.P., μ_a and ρ_a the same coefficients for air, d_1 the length of chamber I. (12·2 cm.), and d_2 the length of chamber II. (49·8 cm.)

$$\frac{p_1}{p_3}\frac{p_3'}{p_1'} = \epsilon^{-\left[\mu\rho d_2\left(\frac{p_2}{\theta}-\frac{p_2'}{\theta'}\right)+\mu_a\rho_a d_1\left(\frac{p_1}{\theta}-\frac{p_1'}{\theta'}\right)\right]\frac{\theta_0}{\Pi}},$$

where p_1, p_3 are the balance pressures in I. and III. with II., full of gas at a pressure p_2 and absolute temperature θ, the symbols with the dash affixed referring to the same quantities with chamber II. at a low pressure; θ_0 and Π being the standard temperature and pressure.

The mass coefficient of absorption for air can be determined by using air in chamber II. μ thus becomes equal to μ_a, and we have an equation with a single unknown. The value so obtained can then be used in the correcting term for other gases. The term involving μ_a is only of the order of 3 per cent., so that an error in μ_a would not affect the other values appreciably.

§3. *Measurement of the Ionization.*

The ionization of the various gases has been measured relative to air under the same conditions of pressure and temperature. The collecting electrodes of chambers I. and II. were connected to the electroscope, that of III. being earthed, and the pressures adjusted so that the gold-leaf remained at rest when the tube was excited. A balance was obtained first with the chamber II. filled with the air, and again when the air had been replaced by the gas under experiment. The ionization in II. is directly proportional to the pressure of the air in I. which is required to balance it. The result is clearly independent of the dimensions of the chambers, and of the intensity of the radiation.

The ionization of the gas in II., however, varies with its temperature and pressure, and for convenience, all the observations were reduced to normal temperature and pressure. Correction is also required for the absorption of the radiation in passing from the collecting system in I. to that in II., since this absorption varies with the nature

of the gas in II. and the pressure of the air in I. (The absorption of the cellophane windows, being constant, does not enter into the calculation.) The path of the radiation was reckoned from the centre of the collecting electrode in I. to the centre of the collecting electrode in II., *i. e.*, 6·1 cm. in air in I., and 12·6 cm. in the gas in II. Since the absorption coefficients are known the correction can readily be calculated. It varies according to the nature of the gas in II. from about 15 per cent. to 30 per cent.

Preparation of the Gases.

As far as possible preparations were chosen which could be carried out *in vacuo*. In this case the whole system could be evacuated to a low pressure and the complete elimination of air ensured. When this was not possible the apparatus was washed out repeatedly with the gas; the chamber being evacuated between each filling.

Air.—The air used both in I. and II. entered the chamber through long tubes packed with soda-lime to remove water vapour and carbon dioxide.

Carbon dioxide.—This gas was obtained from a cylinder. The first portions of the gas from the cylinder were discarded. The gas was dried by calcium chloride.

Nitrogen.—Prepared from sodium nitrite and ammonium chloride. The gas was purified by passing through a mixture of concentrated sulphuric acid and potassium bichromate, potassium hydroxide, and soda-lime, and was dried by calcium chloride and phosphorus pentoxide.

Oxygen.—Prepared by the action of heat on pure crystalline potassium permanganate. It was then passed over solid potassium hydroxide to remove traces of carbon dioxide, and dried by phosphorus pentoxide.

Ethylene.—Prepared by the action of phosphoric acid on absolute alcohol.

Hydrogen sulphide.—Prepared by the action *in vacuo* of water on a mixture of barium sulphide and magnesium chloride, and dried by phosphorus pentoxide.

Nitric oxide was also prepared but was found to attack the insulation so rapidly that measurements were impossible.

§ 4. *Experimental Results.*

The results obtained are given in Table I. The first column gives the value assumed in our calculations for the density of the gas at standard temperature and pressure.

The second column gives the measured mass coefficient, μ, of absorption of the gas for the copper K, radiation. It clearly includes both the true absorption and the scattering. The third column gives the volume ionization of the gas relative to air, that is to say, it gives the ratio of the ionization produced in a given volume of the gas by a given beam of X-rays to the ionization produced by the same beam in an equal volume of air under the same conditions of temperature and pressure. The final column of the table, which is deduced from the previous column, gives the ratio of the ionization of a given mass of the gas to that of an equal mass of air. It thus corresponds to the mass absorption coefficient. The absorption coefficient is an absolute value ; the ionization values are all relative to air.

It will be desirable, at this point, to discuss the probable accuracy of the results given in Table I. It has been

TABLE I.

	ρ_0.	μ.	I_v.	I_m.
Air.....	·001293	9·46	*1·000*	*1·000*
N_2	·001254	7·43	0·743	0·766
O_2	·001429	11·14	1·438	1·301
CO_2	·001965	9·30	1·530	1·006
C_2H_4	·001254	4·32	0·508	0·524
H_2S	·001538	82·7	14·96	12·58

ρ_0=density at N.T.P. ; μ=mass absorption coefficient ; I_v=relative ionization for equal volumes ; I_m=relative ionization for equal masses.

mentioned that the balance pressure can be fixed with certainty to about 1 mm. of mercury. With the pressures usually employed this should give an accuracy of at least $\frac{1}{2}$ per cent. in the values for the balance pressures. The relative ionization depends only on the ratio of the balance pressures and should, therefore, have the same order of accuracy. In point of fact, repeated observations of the relative ionization made with different samples of the same gas did not, as a rule, vary by more than $\frac{1}{2}$ per cent. from the mean value. The values given in the table are the mean of at least four independent experiments. They should, therefore, be correct to at least $\frac{1}{2}$ per cent.

The absorption measurements were not quite so satisfactory. It will be seen from the equation in § 2 that

the coefficient of absorption involves the difference between the logarithms of two balance pressures. With some of the less absorbent gases the change in the balance pressure produced by evacuating the gas from chamber II. did not amount to more than 30 per cent. of the original pressure Discrepancies of the order of 2 or 3 per cent. may therefore be expected between different independent determinations of μ, and variations from the mean of this order of magnitude were in fact found. The values given in the table are usually the means of at least four independent determinations. They should be accurate as far as the first place of decimals. The second decimal figure is probably not significant.

§ 5. *The Total Ionization in Different Gases.*

If a beam of homogeneous X-rays is of such intensity that it produces in a layer of gas having a mass per unit area dm an amount of ionization equal to $I_m\, dm$, the total ionization produced by the complete absorption of the radiation in the gas will be $I_m \int_0^\infty \epsilon^{-\tau m} dm$ or $\frac{I_m}{\tau}$; where τ is the mass coefficient of true absorption. Our experiments give us the relative values of I_m for different gases, and the values of μ the mass absorption coefficient, including the scattering. We have not been able to find any reliable data on the scattering coefficient for copper K_α radiation. For the heterogeneous radiation from a fairly soft X-ray tube it is known that the mass coefficient of scattering, σ, is of the order of 0·2, and is approximately the same for all elements of low atomic number. These results are in agreement with the classical theory of scattering. There is no reason to suppose that the scattering, from elements of low atomic number, increases rapidly with the wave-length, though it is known to increase with the atomic number when the latter is large. Unless the value 0·2 is a gross underestimate, the scattering is such a small fraction of the whole absorption that its exact value becomes of no importance. In the calculations which follow we have assumed that the mass coefficient of scattering for each of the gases used has the value 0·2 and that τ can be calculated by subtracting this amount from the coefficient μ.

The values so obtained for the total ionization in the different gases are given in the first column of Table II.,

the value for air being again taken as unity. (It may be noted that the values so obtained hardly differ by more than the experimental error from those which would be obtained if the scattering correction were ignored completely.) For comparison we give in the second column the values collected by Stuhlman * for the relative total ionization produced in the same gases by the complete absorption of a beam of α-rays from radium. The agreement between the two columns is extraordinarily close, and seems to show quite conclusively that the relative total ionization produced in a gas is independent of the nature of the ionizing agent, even for agents as widely different as α-rays and X-rays.

§ 6. *The average Energy spent per Ion in different Gases.*

The coefficient T, which we have called the relative total ionization, is a measure of the total number of ions produced in the different gases by the complete absorption of the same amount of X-ray energy. Its reciprocal, 1/T, thus measures the average energy spent in producing a pair of ions in the different gases. The values are, of course, not absolute but are relative to that for air, which is taken as unity. It is interesting therefore to compare the values of 1/T, which measure the average energy absorbed in the production of a pair of ions, with the ionization potential P, which measures the smallest amount of energy which will produce a pair of ions. In fact, it was the primary object of our experiments to obtain the data which would enable us to make this comparison, and our choice of gases was governed by this consideration.

Unfortunately, the ionization potentials for the majority of gases available for our experiments do not appear to be known with any great accuracy. The first ionization potential for nitrogen seems to be well established and is given, in the International Critical Tables, as $16{\cdot}7 \pm 0{\cdot}3$ volts. This summarises most of the more reliable experiments sufficiently well. The value for oxygen was originally taken as 15·5 volts, but Mackay † obtained strong evidence for the production of some ionization in oxygen at 12·5 to 12·8 volts. This lower value is confirmed by Smyth ‡

* Stuhlman, Intern. Critical Tables, vi. p. 122.
† Mackay, Phil. Mag. xlvi. (1923); Phys. Rev. xxii. (1924).
‡ Smyth and Stueckelberg, Phys. Rev. xxxii. p. 779 (1928)

by comparing directly the ionization potential in oxygen with that of argon. He states that the ionization potential of oxygen is certainly lower than 15 volts, probably even less than 13 volts. The International Critical Tables adopt the value 12·8 volts for the lowest ionization potential of oxygen, and this is the value we have accepted on the authority of Morris *, whose values for other gases seem to be in excellent agreement with the best data. The values for carbon dioxide and sulphuretted hydrogen rest entirely on the observations of Mackay †, as we have been unable to trace any other measurements of the ionization potentials of these gases. Hydrogen and helium, whose ionization potentials are particularly accurately known, could not, unfortunately, be used in our experiments, as the absorption produced by a 50 cm. column of either of these gases would be far too small to be measured. The values adopted for P, the first ionization potential, are given in the third column of Table II.

It will be seen at once that the total ionization is greatest for gases for which the minimum ionization potential is the least. In fact, the total ionization is not far from being inversely proportional to the minimum ionization potential. The product P.T is given in the last column of the table. For four of the five gases used (oxygen, carbon dioxide, ethylene, and sulphuretted hydrogen) the product P.T cannot be said to differ from a mean value, 14·4, by more than the possible uncertainties in the values of P. This implies that for any one of these gases the average energy absorbed in forming a pair of ions is closely proportional to the minimum energy required to form a pair of ions in the gas. The value of the product for nitrogen is definitely higher than for the other gases, the difference being definitely greater than the possible experimental error. A large amount of work has been published on the ionization potentials of nitrogen, and there seems no reasonable cause to doubt that its value lies between the limits given in Table II. The value for nitrogen is thus the most certain of all the values.

These results raise some interesting points. It is sometimes supposed that the whole of the energy absorbed in a gas is utilized in producing ionization. In this case,

* Morris, Phys. Rev. xxxii. p. 456 (1928).
† *Loc. cit.*

neglecting the ionization produced at critical potentials above the minimum ionization potential, the average energy spent in forming a pair of ions would be very nearly equal to the minimum ionization potential. A theory of the production of ionization by collisions between high-speed particles (α- or β-rays) and gaseous molecules, put forward originally by Sir J. J. Thomson*, developed by Bohr †, and finally corrected by Fowler ‡, suggests that the average energy spent in producing a pair of ions in this way in a gas with a single ionization potential should be equal to 4/3 times the ionization potential. If ionization also takes place at higher critical potentials allowance has to be made for the extra energy required for this process. It is generally believed that the large majority of the ions are

TABLE II.

	T.	T$_\alpha$.	P.	P.T.
Air	1·000	1·00	—	—
N_2	0·982	0·98	16·7±·3	16·4
O_2	1·103	1·13	12·8	14·1
CO_2	1·024	1·02	14·3	14·6
C_2H_4	1·179	1·22	12·2	14·4
H_2S	1·410	—	10·4	14·7

T = relative total ionization from X-ray measurements.
T$_\alpha$ = relative total ionization for α-rays.
P = minimum ionization potential in volts.

formed at the minimum potential §, and that the correction is quite small. It could, of course, easily be calculated if the percentage of ions formed at each potential were known. Neglecting this correction it follows that on either view the ratio of P.T to the energy, E, absorbed should be constant; the ratio P.T/E being unity on the first supposition and $\frac{3}{4}$ on Fowler's theory. It should, therefore, be constant for all gases, except in so far as modification is required by the effect of the higher critical potentials, if this effect is appreciable.

* J. J. Thomson, Proc. Phys. Soc. xxvii. p. 96 (1914).
† N. Bohr, Phil. Mag. xxx. p. 581 (1915).
‡ R. H. Fowler, Proc. Camb. Phil. Soc. xxi. p. 531 (1923).
§ H. D. Smyth, Roy. Soc. Proc. A, civ. p. 121 (1923); A, cv. p. 116 (1924).

The results given in Table II. would thus appear to be in general agreement with the predictions of the theory were it not for the fact that the value of the product P.T for nitrogen is *greater* by some 15 per cent. than the mean value for the other gases employed. The average energy spent in producing a pair of ions in nitrogen is thus less than that for the other gases. The approximately constant value for P.T given by these other gases must be less than the value, $\frac{3}{4}$, indicated by Fowler's theory.

The value of the fraction is, of course, reduced if ionization takes place at higher ionizing potentials, that is to say, if the electron is ejected from a lower level in the molecule. Experiments made with comparatively low velocity electrons indicate that the fraction of the ions produced at the higher levels is small, but this would not necessarily be true for the electrons generated by the absorption of X-rays. Both nitrogen and oxygen are known to have several ionization potentials above the minimum value, and no doubt the same applies to the other gases in the list, although no observations of such potentials appear to have been recorded.

Let k be the fraction of the absorbed energy E (measured in volts) utilized in producing ions with the expenditure of the minimum amount of work, *i. e.*, at the minimum ionization potential P, and k_n the fraction absorbed in producing ionization at a higher potential P_n. The total number of ions produced is given by

$$T = k\frac{E}{P} + \Sigma k_n \frac{E}{P_n}; \quad \frac{PT}{E} = k + \Sigma k_n \frac{P}{P_n}.$$

If the higher terms are negligible and there is no loss of energy by processes other than that of ionization, the value of k should, as Fowler has shown, be equal to $\frac{3}{4}$.

The lack of constancy in the product P.T can be explained by assuming that the energy converted at the higher potentials is appreciable, and differs for different gases, that is to say that the term $\Sigma k \frac{P}{P_n}$ must be taken into account. If, however, the difference between the value of this term for nitrogen and for, say oxygen, amounts to as much as 15 per cent. the term itself must be fairly large, even for nitrogen, as there is no such marked difference in the ratios P/P_n for the higher ionization

potentials as would lead one to suppose that the difference between the terms is likely to be a large fraction of either. If the work spent in producing ions at the higher potentials is comparable with that utilized at the minimum potential, the average value of the energy spent per ion will be appreciably greater than the value (22·3 volts for nitrogen) calculated from Fowler's formula on the assumption that the higher potentials can be neglected, and may quite conceivably be as high as the values suggested (35 volts–42 volts) * by direct thermal measurements on the energy of X-radiation.

On the other hand, it is also conceivable that energy may be lost by the X-ray beam or by the resultant photoelectrons in ways not concerned with the production of ionization, the amount so lost varying with the nature of the gas. It may be significant that nitrogen is the one gas in the table which has no electron affinity. The lower efficiency of the ionization process in these other gases may be connected with their power to attract and capture electrons. The further discussion of these points, however, is not directly involved in the subject matter of the present series of investigations, and is reserved for a separate communication.

Summary.

The coefficient of absorption of copper K_α radiation has been measured for a number of gases. The ionization produced in these gases by a beam of constant intensity has been compared with that in air under the same conditions.

The total ionization produced by the complete absorption of the radiation (relative to that in air) has been calculated. The values so obtained are found to approximate closely to the values obtained for the relative ionizations produced by the total absorption of α radiation.

The average energy expended by X-rays in producing a pair of ions in the gas is found to be approximately proportional to the minimum ionization potential of the gas for oxygen, carbon dioxide, ethylene, and hydrogen sulphide, but is about 15 per cent. smaller for nitrogen.

* Kulenkampff, *Ann. der Phys.* vi. p. 97 (1923). Crowther and Bond, Phil. Mag. vi. p. 401 (1928).

The fraction of the X-ray energy absorbed utilized in producing ionization is approximately constant for the majority of the gases investigated, but is about 15 per cent. greater for nitrogen.

Department of Physics,
University of Reading,
June 1930.

XXX. *On the Measurement of the Sound Transmission of a Partition.* *By* A. E. Knowler, *M.Sc., A.Inst.P.**

IN the Watson † method of measuring sound transmission through a partition a parallel beam of sound is directed towards the partition and the sound intensities on either side are compared. The basis of the Sabine ‡ method of measuring sound transmission is the measurement of reverberation, both in the source room, and in that on the other side of the partition. This paper describes a third method.

Suppose two rooms, A and B, to be separated by an incompletely soundproof partition. Then, if a moving-coil loud-speaker be placed in A and the current through it reduced until the sound is just audible in B, the intensity in the room A is given below by

$$I_A = \frac{4Ki_1^2}{va_A},$$

where

I_A is the sound intensity in A.

K is the constant in the equation $E = Ki^2$, E being the rate of emission of acoustic energy from the loud-speaker and i the current.

i_1 is the current for minimum audibility in B.

v is the velocity of sound in air.

a_A is the absorbing power of the surfaces in A.

If the loud-speaker now be placed in B and the current reduced until the sound is just audible in the same room, we have

$$I_B = \frac{4Ki_2^2}{va_B}.$$

* Communicated by the Director of Building Research, Department of Scientific and Industrial Research.

† F. R. Watson, Phys. Rev. vol. v. pp. 125–132 (1916).

‡ W. C. Sabine, 'Collected Papers on Acoustics,' p. 237.

The reduction of the wall in transmission units is given by

$$10\log_{10}\frac{4Ki_1^2}{va_A}-10\log_{10}\frac{4Ki_2^2}{va_A}$$
$$=10\log_{10}i_1^2-10\log_{10}i_2^2-10\log_{10}a_A+10\log_{10}a_B$$

Similarly, if the experiment be repeated, starting with the observer in A the reduction is given by

$$10\log_{10}i_3^2-10\log_{10}i_4^2-10\log_{10}a_B+10\log_{10}a_A.$$

Any difference between the absorbing power of the two rooms can thus be eliminated, the reduction of the wall being given by

$$10(\log_{10}i_1+\log_{10}i_3-\log_{10}i_2-\log_{10}i_4)$$

In this analysis the energy lost by transmission through the bounding surfaces is considered small compared with the total energy.

Since the observer is absent from each room in turn, the total absorbing power of each room changes. A slab of absorbing material is therefore introduced to compensate for the absence of the observer.

The transmission of a $4\frac{1}{2}$-inch brick wall set in cement mortar has been measured by this method. The transmission laboratory consists of three rooms, the centre one of which is separated from those on either side by test partitions. Shunts of values $\frac{1}{2}$, $\frac{1}{5}$, $\frac{1}{10}$, $\frac{1}{10}$, $\frac{1}{10}$, $\frac{1}{10}$, and a sliding resistance were used to control the current, which was measured with a thermal milliammeter.

The tone used was a "howling tone" of frequency 600 ± 50. Each result given below is the mean of at least six values. To illustrate the variation of the individual values among themselves the following set is quoted: 43·55, 40·34, 43·58, 42·42, 34·70, 38·30. The experiments were spread over several days. Results found on separate days are placed on separate lines.

	Observer 1.		Observer 2.	
	Room A.	Room B.	Room A.	Room B.
	44·0	41·4	44·4	30·6
	44·0	45·8	41·8	35·4
	41·2	44·6	44·2	48·4
	40·8	41·6	42·0	42·2
		46·0		36·2
	40·8	55·2	38·0	42·6
		44·0		46·0
	41·8	43·2	43·4	37·2
		44·4		
Means ...	42·1	45·1	42·3	39·8

The mean of these four values is 42·4 + 0·4 T.U. Davis and Littler *, for a 4½-inch Fletton brick partition measuring 5 ft. × 4 ft. and set in lime mortar, found a value of approximately 44·5 T.U.

The discrepancy between the results of the two observers in room B may be explained by the fact that room B admits a good deal of extraneous noise, while room A is comparatively well insulated. Listening tests in room B are, therefore, more difficult and less accurate. For listening tests made in the quiet room the two observers agree to within 0·2 T.U.

Further tests were made on a fibre-board partition fixed to 3-in. × 1½-in. battens on 2 ft. 0 in. vertical and 2 ft. 6 in. horizontal centres. Each result given below is the mean of six values. Experiments were spread over a period of several days.

	Observer 1.		Observer 2.	
	Room A.	Room B.	Room A.	Room B.
	22·5	20·2	22·5	21·2
	22·5	23·1	21·9	21·0
	21·3	21·5	21·0	20·4
	21·9	20·6	21·2	20·5
	21·5	19·8	21·0	20·5
	20·8	20·4	20·9	20·9
Means ...	21·8	20·9	21·4	20·8

The mean of these values is 21·2 ± 0·2 T.U. The value found by Davis and Littler for a 5-ft. × 4-ft. partition of the same fibre board was 18·3 T.U.

When the position of the source and of the observer was changed, the variation among the readings was no greater than that due to the experimental error when the positions are fixed. Extreme positions were included in these experiments.

The variation of the loud-speaker "constant" over the range of energy input used was negligible.

The method has the advantage that it can readily be applied to the measurement of the sound transmission of the walls in existing buildings. The whole apparatus could readily be made portable.

* Davis and Littler, Phil. Mag., June 1929.

XXXI. *On the Annual Variation of Upper-Atmospheric Ozone.* *By* S. CHAPMAN *.

1. THE annual mean ozone content of the atmosphere, expressed in terms of the thickness of the equivalent layer of pure ozone at normal temperature and pressure, increases with latitude from about 2 mm. at the equator to about 3·25 at Abisko (68° N.). It undergoes a well-marked annual variation, increasing in range from zero at the equator to about 1·5 mm. at Abisko: in each hemisphere the maximum occurs nearly at the vernal equinox (perhaps slightly after, according to the present observations) and the minimum nearly at the autumnal equinox. North of 50° latitude the variation has not been observed through the winter months.

Thus the ozone content C can be expressed very approximately by the formula

$$C = C_0 + C_1 \cos\theta, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ denotes time measured, at the rate 2π per year, from the epoch of maximum C (the vernal equinox); C_0 denotes the annual mean content, and $2C_1$ the annual range, apart from irregular fluctuations. C decreases during the summer half-year, most rapidly at midsummer, and increases during the winter half-year. These changes show that processes of decay and formation of ozone are going on at unequal rates during the year. At present the nature of both these processes is unknown.

2. It has recently been suggested that the main process in the decay of ozone is the normal thermal decomposition, according to the formula

$$2O_3 = 3O_2.$$

The reaction only takes place if the colliding molecules possess energy of activation. If n is the number of ozone molecules per c.c., the number which disappear by this reaction per second may be denoted by kn^2; the recombination coefficient k varies with the absolute temperature T approximately as $e^{-26{,}000/RT}$, according to C. N. Hinshelwood †, and its values at T=300°, 400°, 500° are roughly $1{\cdot}7 \cdot 10^{-25}$, 10^{-20}, $6{\cdot}8 \cdot 10^{-18}$, rapidly increasing with temperature.

* Communicated by the Author.

† 'Kinetics of Chemical Change in Gaseous Systems,' p. 61 (on the basis of Clement's experiments); the value of E, and consequently of k, is somewhat uncertain.

The temperature in the layer where the ozone is densest (about 45 km.) is not definitely known, but there are good reasons for believing it to be at least 300°. The value of n at about 45 km. height may be calculated roughly by supposing the total ozone content to be spread uniformly through a layer 10 km. thick; thus the annual mean value of n increases from about $5{\cdot}5 \cdot 10^{12}$ at the equator to about $8 \cdot 10^{12}$ at Abisko. If T=300° at this level, $kn^2=11$ (at Abisko), and in half a year ($1{\cdot}58 \cdot 10^7$ seconds) the total decrease of n by thermal decomposition would be relatively small; even if T=373° or 100° C., when $k=8{\cdot}5 \cdot 10^{-22}$, thermal decomposition is not very important. If, however, T rises to 400°, though only for a part of each day, thermal decomposition must play a large part in the equilibrium and changes of the ozone.

3. In a recent paper * I have given a tentative theory of these changes, assuming that T is sufficiently below 400° for it to be possible to neglect the thermal decomposition. It has, however, been suggested that T may be high enough for the decay to occur chiefly by this means, and that the rapid decay in the ozone content during the summer may be due to the greater temperature which may then be supposed to exist in the ozone layer. This hypothesis, which at first sight is attractively simple, is here examined.

4. The equation of change of n is

$$\frac{dn}{dt} = \Delta - kn^2, \quad \ldots \ldots \quad (2)$$

where t is measured in seconds, and the rate of increase of n, dn/dt, is expressed as the difference between Δ, which denotes the rate of production of ozone, per c.c. per sec., and the rate of disappearance, kn^2, by thermal decomposition: it is unnecessary at present to consider how the ozone is produced, and Δ may include a portion due to convection or diffusion, from outside, into the volume-element considered, as well as a part due to new production of ozone by dissociation of oxygen molecules into atoms, and their subsequent attachment to other oxygen molecules.

The ozone content of the atmosphere undergoes no perceptible diurnal variation, but this is not necessarily true of Δ, T, and k; however, in considering the annual variation,

* Mem. Roy. Meteor. Soc. iii. No. 26 (1930): an abstract is given in Gerland's *Beiträge zur Geophysik*, xxiv. pp. 66–68 (1929).

it is legitimate to ignore any such daily variations, and to use the daily mean values of Δ and k; the symbols n, Δ, and k are to be interpreted in this sense.

It is convenient to transform the time variable t to θ, given (§ 1) by

$$\frac{\theta}{2\pi} = \frac{t}{365\frac{1}{4}.86{,}400}, \quad \ldots \ldots \quad (3)$$

where the denominator on the right denotes the number of seconds in a year.

Let

$$k = k_0\{1+\phi(\theta)\}, \quad \ldots \ldots \quad (4)$$

$$\Delta = \Delta_0\{1+\psi(\theta)\}, \quad \ldots \ldots \quad (5)$$

where ϕ and ψ are annually-periodic functions with zero mean value, so that k_0, Δ_0 are the annual mean values of k and Δ. If the rate of production of ozone is constant, $\psi(\theta)=0$, but this will not be assumed.

Let the dependent variable n in (2) be transformed to ν, where

$$\nu = n/n_0 \quad \ldots \ldots \quad (6)$$

and

$$n_0 = \surd(\Delta_0/k_0); \quad \ldots \ldots \quad (7)$$

n_0 is clearly the steady value which n would attain if k and Δ had their annual mean values through the year, without variation, because then, by (2), dn/dt would be zero. Hence ν is the ratio of the actual value of n at any epoch, to this hypothetical steady value.

If k were constantly equal to k_0, and if, at time $t=0$, n having the value n_0, the production of new ozone ceased, the decay of n would occur according to the equation

$$n = \frac{n_0}{1+k_0 n_0 t}; \quad \ldots \ldots \quad (8)$$

thus after a time t_0 given by

$$k_0 n_0 t_0 = 1, \quad \ldots \ldots \quad (6)$$

the ozone would be halved; this time t_0 may be called the half-life of the ozone in these circumstances. Let its value expressed in years be s, so that, t_0 being expressed in seconds,

$$t_0 = 365\tfrac{1}{4}.86{,}400s. \quad \ldots \ldots \quad (10)$$

4. Expressed in terms of ν and θ, (2) becomes

$$2\pi s\frac{d\nu}{d\theta} = 1+\psi(\theta)-\nu^2\{1+\phi(\theta)\}. \quad \ldots \quad (11)$$

Now ν is proportional to C, and therefore, by (1), may be written in the form

$$\nu = a_0 + a_1 \cos\theta. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Substituting for ν from this equation, we obtain the following equation involving the unknown quantities ϕ, ψ, and s:

$$-2\pi s a_1 \sin\theta = 1 + \psi(\theta) - \{a_0^2 + 2a_0 a_1 \cos\theta + a_1^2 \cos^2\theta\}\{1 + \phi(\theta)\}, \quad (13)$$

or

$$\{a_0^2 + \tfrac{1}{2}a_1^2 + 2a_0 a_1 \cos\theta + \tfrac{1}{2}a_1^2 \cos 2\theta\}\{1 + \psi(\theta)\} = 1 + \psi(\theta) + 2\pi s a_1 \sin\theta. \quad (14)$$

We suppose that if ϕ and ψ are expanded in Fourier's series, without constant terms (since their mean values, by definition, are zero), *i. e.*,

$$\phi(\theta) = f_1 \sin\theta + g_1 \cos\theta + f_2 \sin 2\theta + g_2 \cos 2\theta + \ldots\ldots \quad (15)$$

$$\psi(\theta) = p_1 \sin\theta + q_1 \cos\theta + p_2 \sin 2\theta + q_2 \cos 2\theta + \ldots\ldots \quad (16)$$

Then equating the constant terms, and the coefficients of the various harmonics, on the two sides of (14), we have

$$a_0^2 + \tfrac{1}{2}a_1^2 + a_0 a_1 g_1 = 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$2a_0 a_1 + g_1(a_0^2 + \tfrac{3}{4}a_1^2) + a_0 a_1 g_2 = q_1, \quad . \quad . \quad . \quad (18)$$

$$f_1(a_0^2 + \tfrac{1}{4}a_1^2) + a_0 a_1 f_2 = 2\pi s a_1 + p_1, \quad . \quad . \quad (19)$$

and so on.

5. At Abisko

$$a_1/a_0 = C_1/C_0 = 0{\cdot}75/3{\cdot}25 = 3/13;$$

hence for latitudes up to 68°,

$$a_1/a_0 \leqslant 3/13.$$

Consequently a_1^2 is small compared with a_0^2, and will be neglected in (17)–(19). Further, since k and ϕ increase with T, which must undergo a simple annual variation, the main terms in (14) must be those of the first harmonic (f_1, g_1), and the later coefficients will be of small magnitude: moreover, the maximum of T and ϕ must occur at or near midsummer, *i. e.*, at $\theta = \frac{1}{2}\pi$ approximately, since θ is measured from an epoch at or near the vernal equinox. Hence f_1 is positive and g_1 is small compared with it: as also are f_2, g_2, ... Thus, in (17)–(19) any terms in which g_1, f_2, g_2, . . are multiplied by the rather small factor a_1 may be neglected in a first approximation. Thus (17) reduces to $a_0^2 = 1$ or

$$a_0 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The interpretation of this result is that, to the present degree of approximation (a few per cent.), the annual mean value of n, which is $n_0 a_0$, is equal to n_0, the steady value corresponding to the annual values of Δ and k.

6. Using (20), and making the approximations already indicated, (19) becomes

$$2a_1 + g_1 = q_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$f_1 = 2\pi s a_1 + p_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The annual variations of n, k, and Δ are all zero at the equator, and increase with latitude, and therefore the same will be true of a_1, f_1, g_1, p_1, q_1. It is convenient to consider the values corresponding to Abisko, where $a_1 = 3/13$.

7. If the maximum of T and k is supposed to occur exactly three months after that of n or C, *i. e.*, at $\theta = \frac{1}{2}\pi$, then $g_1 = 0$. In this case (21) indicates that $q_1 = 2a_1$, *i. e.*, whatever the value of f_1 (which determines the proportionate variation of k) the rate of *production* of the ozone must undergo a proportionate variation at least twice as great as that of n or C. The variation is exactly twice as great if $p_1 = 0$, otherwise it is $\sqrt{(p_1^2 + q_1^2)}$ which exceeds q_1 or $2a_1$.

The variation of Δ represented by the terms $q_1 \cos\theta$ is of a rather improbable kind, because, whatever the value of p_1, it implies a great inequality between the values of Δ in spring and autumn, the ratio being $(1 + q_1)$ to $(1 - q_1)$, or, at Abisko, 19 : 7. It is difficult to see why, in spring, ozone should be produced nearly thrice as rapidly as in autumn, whether the production is due to ultra-violet radiation or to corpuscular action.

But if k has its maximum at the summer solstice, and is equal at the two equinoxes, as supposed, then the necessity for this conclusion, on the basis of the equation (2), is easily seen ; for at the equinoxes n is stationary, and therefore production and destruction just balance ; but in spring n is much greater than in autumn, and the same is true *a fortiori* of the rate of destruction of ozone, kn^2 ; consequently, the rate of production in spring must much exceed the autumn rate.

8. This is so improbable as to preclude the hypothesis here being examined, if it were certain that the annual variation of T and k is symmetrical about the solstices. If, however, the maximum of T and k can occur a month after

the solstice, that is, about four months after the epoch of maximum ozone (though this would be somewhat surprising), the difficulty would largely disappear, and q_1 can be zero, *i.e.*, the rate of production of ozone can have an annual variation symmetrical with respect to the solstices, as would be expected. For then, by (21),

$$g_1 = -2a_1 = -6/13 \text{ (at Abisko)} = -0{\cdot}46.$$

Now, if α is the lag of the maximum of T and k after the solstice (expressed in angle, so that 30° corresponds to one month), $g_1 = -f_1 \tan\alpha$; if $\alpha = 30°$, $g_1 = -0{\cdot}58 f_1$, and since f_1 can be nearly unity if T in winter sinks to a value for which k is much smaller than its summer maximum, the value $g_1 = -0{\cdot}46$ is not an unlikely one.

9. The equation (22) has not so far been used: if the value $a_1 = 3/13$, appropriate to Abisko, is inserted, it becomes

$$f_1 = 1{\cdot}45 s + p_1.$$

This enables an upper limit to be imposed on s, because f_1 and p_1 cannot exceed 1, and whatever their sign, therefore, $f_1 - p_1$ cannot exceed 2. Hence

$$0 < s < 2/1{\cdot}45 = 1{\cdot}38 \text{ year} = 15\tfrac{1}{2} \text{ months}.$$

Since

$$s = 3{\cdot}16 \,.\, 10^{-8}\, t_0 = 3{\cdot}16 \,.\, 10^{-8}/k_0 n_0 = 4 \,.\, 10^{-21}/k_0,$$

for Abisko, taking $n_0 = 8 \,.\, 10^{12}$, this indicates that k_0 must be at least equal to $2{\cdot}9 \,.\, 10^{-21}$, which corresponds to a temperature of about 385° K. This is the lower limit of T for which the present hypothesis can fit the observed annual variation, and this limit corresponds to $f_1 = 1$, $p_1 = -1$; these values are actually not compatible with (20), because if $f_1 = 1$, $p_1 = 1$, then $g_1 = q_1 = 0$: ignoring this difficulty, however, we note that $p_1 = -1$ implies that the production of new ozone is zero at midsummer and has twice the mean value at midwinter (terms in ψ of higher period than the first are here neglected), which is improbable though perhaps not impossible. Until more is known about the mode of production of the ozone and about its annual variation, it is impossible, however, to make the lower limit of T more precise.

10. The increase of C_0 (§ 1) with increasing latitude demands a corresponding increase of n_0 or $\sqrt{(\Delta_0 / k_0)}$: this may be due to an increase in Δ_0, or a decrease in k_0; or to both these causes. If the ozone production is due to ultraviolet radiation, Δ would be expected to decrease with the

latitude (λ), approximately as $\cos\lambda$; if so, k_0 must decrease in proportion to $(\cos\lambda)/n_0^2$, *i.e.*, from the equator to Abisko, in the ratio 1 to 0·14 or 7 to 1 ; if at Abisko $\rho_1=0$, so that k_0 (§ 9) is at least $5{\cdot}8\,.\,10^{-21}$, and T=390°, then at the equator k_0 must at least equal $4\,.\,10^{-20}$ corresponding to T=420° approximately.

The corresponding value of Δ_0 is $k_0 n_0^2$ or $2{\cdot}6\,.\,10^6$, which is a lower limit. If production occurs only during the hours of sunlight, the mean rate during the period of production must be at least twice this, *i.e.*, $5\,.\,10^6$, or, in a layer 10 km. thick, $5\,.\,10^{12}$. This is about one-tenth the number of O atoms which could be produced (at the equator) by the dissociation of oxygen molecules by the sun's ultra-violet radiation, if the effective radiation lies in the band 1300–1800 Å., assumed to have the energy corresponding to the spectrum of a black body at 6000°, and assuming also that each quantum of this radiation dissociates an oxygen molecule ; these assumptions are, of course, doubtful.

11. The results of the preceding discussion may be summarized as follows :—

(i.) Annual mean values and annual ranges of T and k can be assigned which will account for the observed annual variation of ozone, and its observed distribution in latitude, without assuming any annual variation in the rate of production of the ozone. In this case it is indispensable that the maximum of T and k shall occur after the summer solstice by about a month, so that the interval between the maxima of the ozone and the temperature is about four months

This mode of variation of T is somewhat improbable, because the high atmosphere has but little heat capacity and would be expected to adjust its temperature rapidly to the amount of solar radiation received at any time ; thus the maximum temperature should occur very nearly at the solstice, or even, possibly, a little before (if the high temperature in the ozone layer is due to absorption of solar radiation by ozone), because the ozone content is diminishing during the summer. If, however, the temperature at 45 km. is partly determined by large-scale convection, a lag of maximum temperature after the solstice may be possible.

(ii.) If the maximum of T (and k) occurs at the solstice, so that T and k have equal values at the two equinoxes, the observed annual ozone variation requires (on the hypothesis

expressed by (2)) that the rate of production of new ozone shall be much greater in spring than in autumn. This is considered improbable.

The preceding discussion must remain inconclusive until more exact knowledge is attained as to the temperature of the ozone layer. The existing determinations of the height of the ozone layer indicate that half the ozone is below 50 km., and therefore we are concerned mainly with the temperatures at below this level.

The temperatures originally calculated by Gowan for this region are 270° or less ; I understand that later calculations give higher values, but these are not yet published. Whipple* has deduced from the density distribution of the upper atmosphere, calculated by Lindemann and Dobson from meteor data, that the temperature rises from 220° at 30 km. to 380° at 50 km. ; he has also inferred the same value, 380°, for the temperature at about 56 km., from observations of the abnormal audibility of sounds from gunfire during the summer of 1928 †. These inferences are, however, admittedly very uncertain, and it seems rather improbable that the temperature gradient should be so very rapid in this 20-km. layer ; the temperature at the level 30 km. is known by actual observation to be about 220°. The highest estimates of the temperature between 40 and 50 km. are near the point where the thermal decomposition of ozone rises to importance, according to the present laboratory data, which also, unfortunately, are somewhat uncertain. It is therefore very desirable to confirm or disprove these estimates, and also, if possible, to determine whether the temperature undergoes annual and diurnal variations (and, if so, with what amplitudes and phases) ; a diurnal variation would be of great importance if it raised the temperature to about 400° even for only a short part of the day ; it may be remarked, however, that if there is an appreciable daily variation it is unlikely that the annual maximum of temperature will lag by so much as a month after midsummer. I understand that observations of the abnormal propagation of sound do not suggest any diurnal variation of temperature at about 50 km.

* 'Nature,' Aug. 28, 1926.

† Gerland's *Beiträge zur Geophyzik*, xxiv. p. 75 (1929).

XXXII. *A Design for a very large Telescope.* *By* E. H. Synge *.

RESULTS which were formerly looked upon as requiring the construction of a very large curved surface are obtained in Michelson's method of stellar interferometry by the superposition of reflexions from small surfaces. It seems possible to extend this idea to the purpose of light-gathering, instead of resolving, power.

A form of telescope will be suggested in which a number of moderate-sized parabolic reflectors perform the functions of a single very large reflector. Theoretically, at least, this form of telescope could be made to give virtually the same degree of resolution as a telescope with a single large reflector, of surface area equal to the combined areas of the assemblage of small reflectors. But to do this it would have to be made and adjusted with very great refinement, and with the best atmospheric conditions which are met with in the temperate latitudes this refinement would be wasted. It seems that ·6″ may be taken as the minimum angular diameter of the photographic image of a star, which can be obtained by any of the large telescopes in the United States; and in the case of a very large telescope (from 3 or 4 metres in aperture upwards) it is improbable that the best visual image can be much less than the photographic. This limit is imposed by the minimum of atmospheric disturbance over the area; and if a very large telescope is designed for use in that area, so that under the steadiest atmospheric conditions to be met with it will give a photographic image of approximately ·6″, there is no advantage in carrying refinements of design and construction any further.

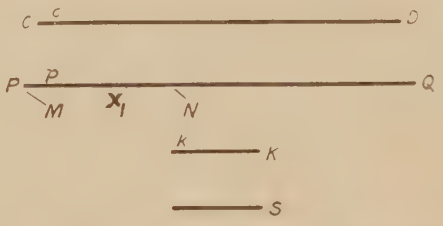
There is a considerable gain in simplicity in limiting the discussion to a telescope which will obtain this result, but does not aim at a greater theoretical efficiency; and we will first discuss the design with this limitation. Afterwards we can consider the possible use of a higher theoretical efficiency, and how this could be obtained.

The design consists essentially in the assemblage of a number of similar reflecting telescopes pointed in the same direction, the images from which are ultimately superimposed in the focal plane of another reflector or lens S, the

* Communicated by the Author.

resultant image containing the aggregate light of all. If the assemblage contains n^2 reflectors each of 1 metre aperture, it will be shown that the resultant image of the field is virtually identical with that which would be formed by a single reflector n metres in diameter and having a focal length whose ratio to aperture is slightly greater than this ratio in the case of S. The field is indeed more restricted, and some light is lost by additional reflexions and transmission through a lens. But there are many compensating advantages.

The diagram below shows a schematic cross-section of the arrangement.



The n^2 parabolic reflectors are arranged within a circle of which PQ is a cross-section. n^2 corresponding Cassegrainian reflectors are represented by CD. The whole assemblage forms a sort of "battery" of n^2 1-metre telescopes, all pointing in the same direction. S is a large lens, or reflector, of, say, 1 metre in diameter. K is the cross-section of an assemblage of n^2 collimating lenses, each of a little less than $\frac{1}{n}$ metre in diameter and set together as closely as possible. I is the image of the field formed by p, a parabolic reflector at the left-hand side of the assemblage, the rays incident on p being reflected, first, to the Cassegrain reflector c, then emerging through a hole in p, whence they are reflected by a plane mirror M to I. We are only concerned with a limited area of I, in the centre of the field, the remainder being cut out by a diaphragm or the walls of a tube. The rays after passing through their foci at I are reflected by a parallel plane mirror N into k, one of the collimating lenses at K. M and N are adjusted so that I or, to speak more accurately, its reflexion, is in the focal plane of k, and the rays will consequently emerge from k as parallel beams, and, striking S, will form an

image of the field in the focal plane of S. It can easily be seen that this image is a magnification by a little more than n diameters of the image of the field which would be formed if S were used directly as an objective. The parallel beams incident on p have, in fact, been converted into parallel beams issuing from k, and the latter have somewhat less than $\frac{1}{n}$ the diameter of the former. There will, therefore, according to the general law which governs such reductions, be a corresponding increase in all angular divergencies.

We have dealt with one parabolic reflector p and the rays which fall upon it. A precisely similar arrangement is made in the case of every other member of the assemblage. To any other parabolic reflector p' corresponds a Cassegrain reflector c', two plane mirrors M′ and N′, and a collimating lens k', which ultimately conduct the rays incident upon p to an image in the focal plane of S. This image of the field is precisely similar to that formed by the rays coming from p, and if the apparatus is properly adjusted, will be directly superposed on it. Owing to the "boiling" effect of atmospheric disturbances, we may consider that there are no special phase relations between the two superposed images, the resultant effect being simply additive. The n^2 parabolic mirrors at PQ will thus form n^2 identical superposed images of the field in the focal plan of S, the resultant image containing, at all events near the centre of the field, all the light which is incident upon the n^2 parabolic mirrors, except the fraction which is lost in the reflexions and in transmission through the lenses. Except for this loss, the image of the field will be virtually identical in all respects with that which would be formed by an objective n metres in diameter, and having a slightly greater ratio of focal length to aperture than S. This is true, however, only within a limited region near the centre of the field, and we have still to consider how large this region may be. We need not consider curvature of the image-surface at I as this can be compensated for elsewhere.

If the parallel beam which emerges from the collimating lens k is the full breadth of the lens, it is clear that, if there is to be no loss of light, only the poi t in the exact centre of the field will be properly provided for. The images will deteriorate as we pass outwards fr m the centre. It

would probably be best that the parallel beams emergent from k, and the other collimating lenses, were a little less in width than the lenses, and thus the images should be equally good over a small region in the centre of the field. We may take that portion of I. from which a tolerably good image can be obtained, as a circle of about one-half the diameter of the collimating lens, there being some deterioration towards the boundary of this circle. If k is a little less than $\frac{1000}{n}$ mm. in diameter, and if we take 10 mm. in the image I as equivalent to a minute of arc of the field, the effective field would be some $\frac{50}{n}$ minutes of arc in diameter, or 5 minutes of arc when $n = 10$. The dimensions of the effective field can be increased by increasing the size of S, and hence of k. Thus, if S were 2 metres instead of 1 metre in diameter, the effective field would be 10 minutes of arc in diameter. The field could also be increased if there were an assemblage of lenses, instead of reflectors, at PQ. Indeed, there would be many advantages in having objective lenses instead of mirrors here. The writer has limited himself to reflectors only because the expense of an assemblage of 1 metre lenses would probably be prohibitive. The best results of all, and the largest effective field, could probably be obtained, if expense were not in question, by an assemblage of lenses at PQ and a large doublet lens at S. In the case of reflectors the focal lengths of p (diagram, p. 354) should be made as short as possible. If S were a reflector, it might be more convenient that it should face in the opposite direction, with, of course, a corresponding modification of the arrangement of the plane mirrors and collimating lenses. Many other modifications would probably suggest themselves to anyone constructing an actual instrument. The aim of the present paper is only to suggest the general method in broad outline.

As regards the arrangement of the plane mirrors, care would be taken that the mirrors and diaphragms, or tubes, which served one beam should not cut across the path of any other beam. It is necessary, also, that the light from one beam should not enter any collimating lens but that designed for it. As well, therefore, as a diaphragm at I, delimiting the field, there should be a diaphragm near I, which would cut out all light except what would enter the

proper lens. There does not seem to be any particular difficulty about these details, as one has the widest latitude in all the arrangements. It may be remarked also that there need not be any members of the assemblage PQ near the centre of PQ. They could be arranged in an annular form if this were more convenient for the arrangment of the plane mirrors.

All the component parts would, of course, be carried on a lattice metal framework. This could be made tubular, and air circulated through it, so that there would be no differential temperature effects. If necessary, there could also be provision for temperature compensation in the frame. So far as the effect of temperature is concerned, a composite telescope of this kind should be much superior to one with a single very large reflector, supposing this could be constructed of equivalent size. The superiority would be still more marked as regards weight and convenience, for the weight of such a telescope would tend to increase as the square of the equivalent aperture, while that of an ordinary telescope would increase as the cube.

Hitherto we have considered the case of a composite telescope in which we could look upon the beams contributed by the various members of the assemblage PQ as quite independent of one another. It was merely necessary to make the adjustments so that the n^2 images in the focal plane of S were exactly superposed on one another. In spite of any appearance of complexity in the arrangement, there was so much latitude in planning the details that there did not seem to be formidable difficulties of any kind in constructing such an instrument, even of a very large size with light-gathering capacity quite beyond anything possible in the case of a telescope with a single large reflector. But the difficulties would become much more formidable if the attempt were made to construct such a telescope, which would yield the full resolving power of its equivalent aperture. To justify the consideration of such a telescope, it seems necessary to turn our attention to the question of atmospheric disturbances, and see whether we must take ·6″, or thereabouts, as a definite limit to the photographic resolution, or whether we might hope, in any cases, to pass beyond it.

In the lower atmosphere, and up to a considerable height, there are, in most places, days of almost complete calm;

but meteorologists seem to be in agreement that, in the temperate latitudes, there is a perpetual west wind at a very great height, blowing with a velocity of 60 miles per hour, or upwards. This constant wind, which is connected with the rotation of the earth, seems quite sufficient to account for the limit of ·6″, which corresponds with the calmest conditions of the lower atmosphere. If we wish to pass beyond this limit, we must therefore find some latitude where there is no such strong constant wind at great heights. At the Equator the Krakatoa dust revealed a constant *East wind* of about 60 miles an hour, at a great height. We might, therefore, fairly expect to find a zone between the Equator and the temperate latitudes where the winds in the higher atmosphere were much less strong, and probably indeterminate in direction, with occasional periods of almost complete calm. One would expect the same thing in the Polar regions, for any winds depending on the rotation of the earth must become indeterminate in direction as we approach the Poles. We know, indeed, that there are periods of almost complete calm in the Antarctic regions. C. G. Simpson in 'The Meteorology of the British Antarctic Expedition, 1910–13,' vol. i. p. 133, records occasions when the smoke from Mount Erebus (4000 metres) "rose so vertically that no direction could be assigned to it. This means that the air through a great thickness was for all practical purposes absolutely still; and yet this phenomenon was observed four times in twelve months." He also mentions one occasion when a balloon was sent up, and an instrument detached when it had risen 4000 metres. The balloon ascended almost vertically, and after 25 minutes the instrument was seen to fall within 100 metres of its starting-point. There do not seem to be any reasons why this state of almost absolute stillness should not extend to the very highest portion of the atmosphere in these latitudes. So that, both here and, possibly, also in a zone in the tropical or subtropical latitudes, there may be a few days in the year when a resolving power far in excess of anything practicable in the United States could be brought into play. It is not, therefore, of merely theoretical interest to show that the type of telescope suggested is available for a great resolving power, and that, if the workmanship and adjustments are perfect enough, the various beams can be made to combine in such a way that

the effect is not merely additive, but that they should yield the full resolving power of the equivalent aperture.

Let us first suppose that the arrangement of the parabolic reflectors (or lenses) at PQ is exactly similar to the arrangement of collimating lenses at K. Thus the collimating lens corresponding to any given member of the assemblage at PQ occupies precisely the same relative position in the arrangement at K as the member in question in the arrangement at PQ. We may suppose that the members of the assemblage at PQ, and also the collimating lenses, are all set together as closely as possible, and that the beams issuing from the latter have the full breadth of the lenses, which means, of course, that we confine ourselves to the consideration of a star directly on the axis of the instrument. The adjustments are assumed to be of such accuracy that the path-lengths of the n^2 beams are all optically equal when they meet in the focus of S.

Under these circumstances it can be seen that the total beam which proceeds from K to S is virtually the same as would be obtained by converting (by any ordinary system of lenses or reflectors) the beam incident upon a single reflector, of area equal to the combined areas of the assemblage at PQ, into a parallel beam of the breadth of S.

The diffracted rays of the n^2 constituent beams which proceed from L to S, in fact, tend to combine and cancel one another out. One can apply to the consideration of the question the very general argument which Schuster and Nicholson use in connexion with Michelson's stellar interferometer.

What has been said refers only to a star on the axis of the telescope. To make the instrument available for a larger field, it would be necessary that the beams issuing from the collimating lenses at L should not have the full breadth of the lenses. The members of the assemblage at PQ would, then, not be arranged as closely together as possible; but the diameter of any member of the assemblage should bear to the distance between its centre and the centre of any other member the same ratio as is borne by the diameter of a beam emerging from a collimating lens to the distance between the centres of the two collimating lenses corresponding to the two members of the assemblage at PQ, which are in question.

Thus, theoretically, at least, over a limited field, it

appears possible to obtain the full resolving power of the equivalent aperture ; although it is unnecessary to enlarge on the refinements of workmanship which would be needed to secure this in practice, in the case of a very large telescope.

When the writer had nearly completed the present paper, he came upon a suggestion by E. E. Fournier D'Albe * for a " composite telescope " which at first seemed to him to be essentially the same as that developed above. From the context, however, it appeared that Dr. Fournier D'Albe looked upon the resolving power as dependent upon the focal length of the constituent lenses or reflectors : and this the present writer did not understand. But what finally convinced him that Dr. Fournier D'Albe must have had some quite different idea in view was the fact that his suggestion was put forward as the converse of a suggestion for a searchlight or beacon in which a large number of very small carbon arcs were to be used with a corresponding number of small reflectors. Now, the converse of the idea which has been developed in the present paper is obtained by placing a *single* carbon arc of ordinary size in the focus of S. A beam with very small angular divergence will then emerge from the assemblage PQ.

Quite apart from the possiblities of the arrangement suggested for telescopic purposes, a useful application of it might indeed be found —with some obvious modifications —in a searchlight or beacon of very small angular divergence, and hence of great intensity at a distance.

XXXIII. *Notices respecting New Books.*

Mechanics of the Gyroscope. By E. F. Deimel. (The Macmillan Co., New York. Price 17*s.* net.)

THIS work, the latest addition to the Engineering Science Series, edited by Prof. D. C. Jackson, of the Massachusetts Institute, and Prof. E. R. Hedrick, of the University of California, has been primarily written to provide an introduction to the study of gyroscopic phenomena and the numerous and varied applications in modern engineering. The first three chapters of the book are entirely mathematical, and deal with plane motion, motion in space, dynamical laws, and the general equations of rotation : numerous exercises are introduced, some fully worked out, others

* E. E. Fournier D'Albe, 'The Moon Element,' p. 88 (1924).

with hints as to the methods of solution. In the remaining chapters, the author gives a clear and concise treatment of typical gyroscopic devices: a detailed description of the behaviour of gyro-compasses and their use in automatic steering—the three graphs at the end of the ninth chapter show in a striking way the superiority of gyro-pilot steering—and the theory of gyro-stabilizers, the one invented by Schlick a quarter of a century ago and the active type of stabilizer introduced by Sperry. Prof. Deimel's book can be cordially recommended as a preparation for the study of the more advanced texts and the discussion of the new problems, such as the whirling of shafts, which have arisen with the introduction of high-speed machinery.

The Universe around Us. By Sir James Jeans. (Cambridge University Press, Fetter Lane, London, E.C. 4. Price 12*s.* 6*d.* net.)

In writing this book, Sir James Jeans had in mind the needs of the reader with no special scientific knowledge, and, dispensing with mathematical analysis, has given an able survey of recent astronomical advances, especially the researches of Prof. Shapley and Dr. Hubble on globular clusters and spiral nebulæ, whose distances are measured in millions of light years, and the equally remarkable researches in the structure of the atom. It was a remark of Pascal's that "Man should learn to estimate the earth and the heavens. Then let him take some small creature and observe its minute structure: has he found the least thing in Nature? I will show him a depth beyond. Not only this world but all that we can conceive of the world may exist within the limits of an atom. He who reflects after this manner will realize that he is supported between two infinities: he will contemplate in reverent silence the wonders of which he is a part."

In discussing the internal constitution of the stars, the author introduces the hypothesis that the central regions may properly be described as in the liquid state, and for the source of stellar energy the hypothesis of the annihilation of matter. Of particular interest are the fine photographs of nebulæ, planetary, galactic, and extra-galactic, taken at the Mount Wilson and Yerkes Observatories, the series of three Lowell Observatory photographs of Saturn, and the photographs of the tracks of α and β particles taken by Prof. C. T. R. Wilson and Mr. P. M. S. Blackett.

Soap Films. By A. S. C. Lawrence. (G. Bell and Sons, Ltd., York House, Portugal Street, Kingsway, London, W.C. 2. Price 12*s.* 6*d.* net.)

The author has drawn on his wide experience in the Royal Institution, where he acted as Assistant to the late Sir James Dewar, and has produced a very complete account of the

preparation, manipulation, and behaviour of soap films. In a Foreword, Sir William Bragg commends this book, which is not only a record of practically acquired knowledge, but a detailed summary of the researches on films carried out during the last thirty or forty years. References are given to the earlier work of Reinold and Rücker, the numerous experimental results obtained by Dewar, and to the latest work of McBain, P. V. Wells, and others. Mr. Lawrence has repeated some of Perrin's experiments and has written an interesting account of stratified films and the theories of the constitution of the black film. Four important papers referred to in the text were published in the 'Philosophical Magazine': Lord Rayleigh, on thin oil films on water (this study having a direct bearing on the nature of soap films); Johonnott, two papers on the thickness of the black film; Naranyan and Subrahmanyan, on the surface-tensions of sodium oleate solutions; and de Noüy's researches on soap solutions at extreme dilution. The author summarizes much of the experimental work of Freundlich on the determination of surface-tension and on solutions with threadlike colloid particles, and Lascary's investigations of the lowering of the surface-tension of water by the sodium salts of the fatty acid series. A considerable number of graphs and tables of numerical data are given in the book; the preparation of pure oleic acid is described in an Appendix, followed by a table of measurements of the thickness of soap films. The beautiful photographic plates of soap films, especially the coloured microphotographs of stratified films forming the frontispiece, add much to the value of this book.

An Introduction to Modern Organic Chemistry. By L. A. Coles, B.Sc., A.I.C. [Pp. xv + 452, with illustrations and 77 figures. (London: Longmans, Green & Co., 1929. Price 7*s.* 6*d.*]

The requirements of the examination for Higher School Certificates and of other examinations of this standard are covered by this book. It combines theory and practice; a large number of experiments, which have been selected with care, are described in detail. The book is divided into three parts. The first deals with the properties and reactions of ethyl alcohol and acetic acid, and is largely experimental. The second part is concerned with aliphatic compounds, and introduces considerations with regard to molecular structure and molecular changes during reactions. The third deals similarly with aromatic compounds. The principal stages in the development of organic chemistry are summarized in a final historical chapter.

Type of two sizes is used, the smaller size being intended to be passed over at a first reading. Questions are given at the end of each chapter. In spite of a few errors, which should be corrected in a second edition, the book can be recommended as suitable for school use.

Algebraic Geometry and Theta Functions. By Arthur B. Coble. American Mathematical Society Colloqium Publications, vol. x. [Pp. vii + 282.] (New York: American Mathematical Society, 1929. Price $3.00. English agents: Bowes & Bowes, Cambridge.)

This monograph contains, in amplified form, the Colloqium Lectures delivered at Amherst in September, 1928, under the title "The determination of the tritangent planes of the space sextic of genus four."

The first two chapters are introductory and give an outline of those topics in algebraic geometry and theta functions which are necessary to the understanding of later applications. The succeeding three chapters deal with the geometrical applications of the functions of genus two, genus three, and of Abelian modular functions of genus four respectively. The final chapter, on theta relations of genus four, gives Schottky's solution of the tritangent plane problem when the sextic lies on a quadric cone.

Schottky, with the theta relations as a starting point, defines a few sets of points in terms of theta modular functions of genera two, three, and four. The author's method is to develop the properties of discrete sets of points in projective spaces, congruent to each other under regular Cremona transformations. Such sets have associated groups which are isomorphic with theta modular groups. The two methods of treatment are correlated by means of a theorem proved in this volume that the sets defined by Schottky are transformed under period transformation of the moduli into sets congruent to the original set under Cremona transformation.

As a summary of the work which has been done in combining theta function theory with algebraic geometry the volume is excellent. The type and general arrangement are worthy of commendation.

Coal Measure Plants. By R. Crookall, Ph.D. [Pp. 80, with frontispiece and 39 plates.] (London: Edward Arnold & Co., 1929. Price 12*s.* 6*d.* net.)

Fossil plants provide the best and sometimes the only criteria by which different coalfields may be correlated with one another, and serve also in some instances to correlate individual seams. Dr. Crookall, who is palæobotanist to the Geological Survey of Great Britain, has written this book to serve as a brief introduction to the palæobotany of the British Coal Measures; it is not written primarily for the specialist, but it is intended for the use of students of botany, geology, and mining, and of amateur naturalists.

After a general introduction dealing with types of fossilization and plant divisions in the Coal Measures, brief descriptive notes are given on 240 of the more common and characteristic British

Coal Measure plants. Rare forms have been included only where they are characteristic. Figures of all these plants are given in the excellent series of plates.

This book should do much to facilitate the identification of species by the non-specialist. Amateur collectors have in the past contributed considerably to the subject, but the complicated nomenclature is perhaps responsible for interest fading. It is to be hoped that Dr. Crookall's work will help to remedy this state of affairs. Some useful practical hints to collectors are given in an appendix.

An Introduction to the Chemistry of Plant Products. Vol. II. *Metabolic Processes.* By Paul Haas, D.Sc., Ph.D., and T. G. Hill, D.Sc., A.R.C.S. Second Edition. [Pp. viii + 220, with 12 figures.] (London: Longmans, Green & Co., 1929. Price 10*s.* 6*d.* net.)

The second volume of Haas and Hill's Chemistry of Plant Products deals with metabolic processes in the living plant. The subjects dealt with include the synthesis of carbohydrates, of fats and of proteins, respiratory processes, and growth. The increasing importance of these subjects and the large amount of research done on them since the publication of the first edition in 1922 have necessitated much revision and rewriting. This task the authors have carried out with marked success, and no work of importance up to the date of publication has been omitted. The treatment throughout is clear and concise, and full references are given to original papers. A subject-index is given, but not an author's index.

The Effects of Moisture on Chemical and Physical Changes. By J. W. Smith, B.Sc., Ph.D. (Text-Books on Physical Chemistry.) [Pp. xii + 235, with 44 figures.] (London: Longmans, Green & Co., 1929. Price 15*s.* net.)

An extensive literature has accumulated on the influence of intensive drying on chemical and physical properties. No connected account of the work which has been done on this subject has hitherto been available. Dr. Smith's book therefore fills an important gap.

After a general historical survey, which includes references to the effects of traces of water-vapour on chemical reaction dating back as far as 1780, the effects on chemical changes are considered. These are discussed in the order: gaseous reactions, solid-gas reactions, reactions between solids, reactions in non-aqueous solvents, the decomposition of solids and miscellaneous effects. To the more important reactions, such as carbon monoxide-oxygen and hydrogen-chlorine, a whole chapter is devoted. The experimental procedures are frequently given at some length,

and the different theories which have been proposed to account for the phenomena are summarized. The effects of intensive drying on physical properties are then considered in detail. All investigations up to 1929 have been included.

As a compilation the work is excellent, but a more critical discussion of the material, both on the experimental and on the theoretical sides, would have been of value. The experimental evidence is not all of the same weight, and conclusions are apt to be misleading if this is not expressly pointed out.

Many theories have been put forward to explain the various phenomena. No one theory has gained universal acceptance, and it is probable that no single theory is applicable to every case. A critical discussion and inter-comparison of the several theories would have added to the value of the work. Students of physical chemistry will be greatly indebted, nevertheless, to Dr. Smith for his account of the work which has been done; full references to original papers are given throughout, so that these can always be referred to for further details.

La Gamme—Introduction à l'étude de la musique. Par P. J. Richard. [Pp. 231.] (Librairie Scientifique, Hermann et Cie, Paris. Price 28 fr.)

Monsieur Richard wrote this book primarily for the benefit of his daughter, who was studying music, in order to give her and other students a clearer knowledge of the fundamental facts of the subject. It is an account of the various musical scales, and it is treated very lucidly, the fundamental likenesses between the scales being plainly indicated.

The first chapter introduces Arithmetic and Algebra. This groundwork illuminates acoustical facts occurring in the other chapters of the book. Thus, students of music, when they follow the course laid out in this book, ought clearly to understand the various symbols.

The next four chapters are given up to a full explanation of the various scales adopted in Europe, ending with a table of comparison between four of them, including the scale of Pythagoras.

Chapter V. is devoted to the Physical significance of the scales and such properties of sound as pitch or frequency, intensity, and quality. Simple harmonic motion is expounded graphically, and the place of partials, natural and artificial, is also illustrated.

The method of modulation and transposition is explained with reference to the various scales, and the discrepancies emphasized.

Various musical instruments are described, a chapter being devoted to the organ-pipe. In every case the laws of vibration, transverse and longitudinal, are stated and discussed. The notes of the scales which occur as partials in the different cases are shown on the systems in which they appear.

The book ends with a note of regret that modern music seems to be degenerating into a jumble of noises without any attention being paid to discord or concord.

The subject is dealt with in a very competent manner, the illustrations are sufficient and clear, and the whole arrangement is good.

Beyond Physics. By Sir Oliver Lodge. [Pp. 172.] (George Allen & Unwin. Price 5*s*.)

At a period when doubt is so much abroad that uncertainty has been elevated into a principle, it is well that we have among us one who is not only not afraid to examine the wide problems that lie beyond physics, and in particular the age-old questions of the nature of life and mind, but who also has an intellect sufficiently comprehensive to formulate a general plan and an unrivalled mastery of graphic phrase to expound it. Sir Oliver Lodge brings to the discussion of the relationship between spirit and matter an experience of things physical and spiritual which is not to be matched. In physics he combines a profound knowledge of the old with a keen appreciation of the new, while his professional acquaintance with the properties of matter has progressively strengthened his faith in a common basis for the material and the non-material. Anything which he has to say on a subject of such fundamental importance as the nature of life is properly addressed to a very wide public, but it is, perhaps, of particular interest to physicists to follow the bold arguments by which Sir Oliver makes the latest and most revolutionary aspects of physical theory the basis for a general scheme of psychical reality, and amalgamates the problems of the propagation of light and the purpose of life into one.

The fundamental substance—for Sir Oliver calls it a "continuous substance"—of Sir Oliver's scheme is the ether of space, a conception which has undergone many vicissitudes, as can be seen from Professor Whittaker's 'History.' Sir Oliver freely acknowledges that the old "mechanical or engineering ether" as he calls it, with one of his happy phrases that condense many ideas into a few words, is extinct, but he has a vivid conception of a medium "far less familiar but more accommodating" in its place. This conception is more or less intuitive, a matter of direct apprehension: Sir Oliver alludes to certain sources of information not accessible to the physicist as such, but does not invoke them in his exposition. "I postulate, then, as the one all-embracing reality on the physical side, the Ether of Space. And I conceive that in terms of that fundamental physical entity everything else in the material universe will have to be explained." It is the

first step that is likely to prove one of the most difficult for the sceptical physicist who has replaced the sceptical chymist of Robert Boyle. Sir Oliver's conception of the ether is astonishingly vivid. It has for him that quality of reality which makes it a suitable medium for the expression of his ideas; as Faraday, no doubt, "saw" his lines of force, so Lodge sees the ether. There is no doubt that any genius progressing along difficult and unexplored paths must have some brilliant torch of this nature to illumine his way, and if it enables him to advance towards the truth it needs no other defence. Although he may not be able to hand it to certain others, this limitation of its usefulness does not, and should not, prevent all benefiting by any discoveries made by its light.

Sir Oliver's ether is a difficult conception. He speaks of it as containing ultra-microscopic vortices circulating or spinning with the velocity of light, and elsewhere of variety of circulatory movement, and of a constitutional turbulent or rotational velocity of the ether. It is hard to think of a vortex motion denoted by one fixed linear velocity, nor, in spite of his insistence on it, does this turbulent velocity seem essential to Sir Oliver's scheme. Elsewhere it appears that ether and space are almost synonymous, yet we have to imagine discontinuities, hollows, in it to represent particles. Sir Oliver's position may well be that the conception of the ether, being the key to the whole life problem, is likely to remain obscure, and, perhaps, not amenable to close analysis, for some time, and that he puts forward this ether as a pictorial, and not necessarily self-consistent aid, rather than as an entity subject to mathematical laws: he may contend that a vividly apprehended ether is a nearer approach to reality than a system of equations without humanity. Such a view would command assent in many quarters.

Having made the ether a plausible reality to any but the most censorious and cynical reader, Sir Oliver proceeds to expound the elements of wave mechanics, and more particularly the connexion between the group velocity—corresponding to particle velocity—and the wave velocity in the hypothetical dispersive medium of de Broglie and Schrödinger. In this discussion he displays to the full that critical acumen and incisive phrase, that gift for illuminating analogy, which make all his physical work so stimulating. For many the dispersion waves, or constituent waves, are provisional mathematical fictions, and it would appear that to Schrödinger himself they are little more, but it is of fundamental importance to Sir Oliver's thesis that they should be an abiding reality and "the substratum of everything." They direct, he points out, but leave no experimentally accessible record, and have no energy of their own. "Are not," he asks boldly, "these the

kind of assertions which we have been constantly making about life?" His far-reaching hypothesis is that these ether waves are the physical basis of life and mind. For the development of the new theory, and the daring arguments by which it is supported, we must refer readers to the book itself.

The critic may say that the conception of the ether put forward is not self-consistent, and that the argument depends entirely upon analogies. It seems to us a sufficient answer that in an attempt to solve, or to adumbrate a solution of, a fundamental question of such magnitude and difficulty minor contradictions cannot be avoided, and that beyond analogy and direct apprehension there are no weapons available. We commend this extraordinarily acute and persuasively-written book to all who take an interest in what lies outside and beyond physics. E. N. DE C. A.

XXXIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. ix. p. 1200.]

May 14th, 1930.—Prof. E. J. Garwood, M.A., Sc.D., F.R.S., President, in the Chair.

Mr. F. A. BANNISTER exhibited lantern-slides to demonstrate the identification of minerals in thin sections of rocks by X-ray methods. Laue photographs of supposed nepheline in small phenocrysts in kenyte from Mount Kenya were shown, and compared with a Laue photograph of a nepheline-crystal from Monte Somma, Vesuvius. These photographs confirm the presence in kenytes of nepheline as phenocrysts. This problem, suggested by Mr. W. Campbell Smith, illustrates the use of X-ray methods for identification of minerals in thin sections, where the separation for chemical analysis of the constituents which are being examined is too difficult: this work is in a preliminary stage. For phenocrysts not oriented so favourably, Laue photographs are in some cases to be supplemented by oscillation photographs. The information recorded on X-ray photographs is considerable. In addition to determining minerals, the mutual orientation of two individual crystals may be obtained, the twin-law (if any) deduced, and accurate values for the axial ratios and unit cell-sides calculated. Photographs have been obtained for crystals of the order of 0·1 mm. in diameter. For the ground-mass of some finer-grained rocks the powder method would probably yield a solution.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]